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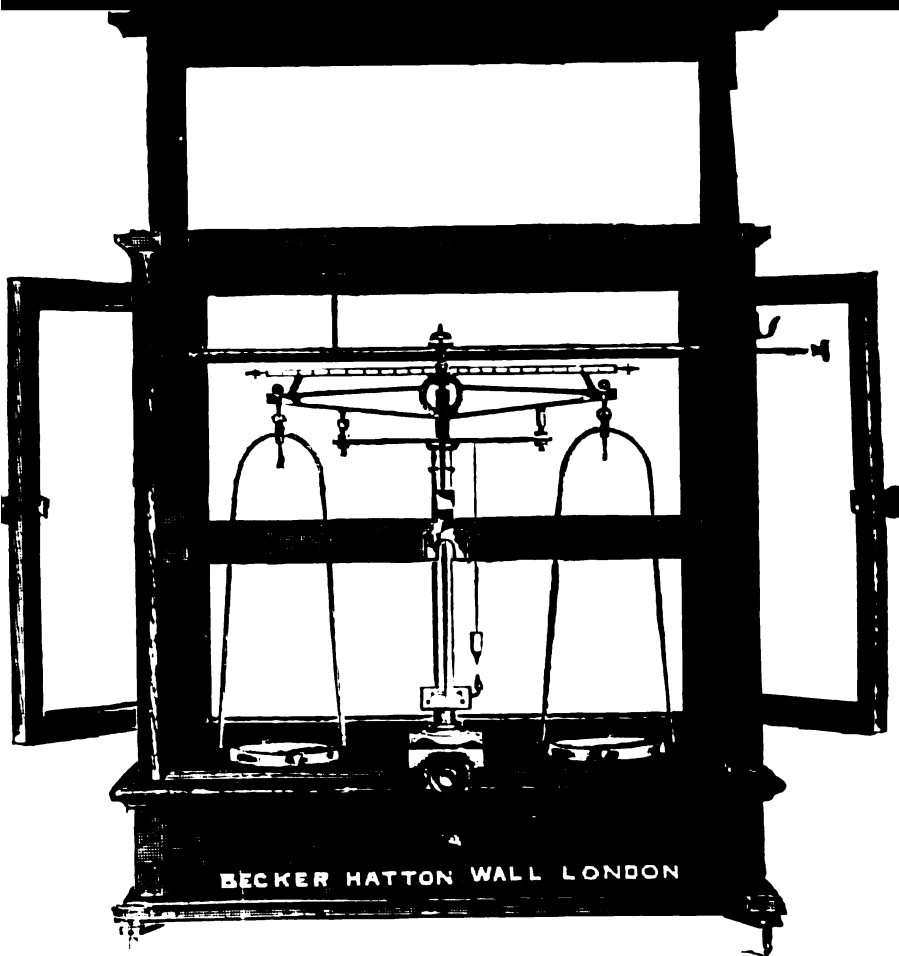
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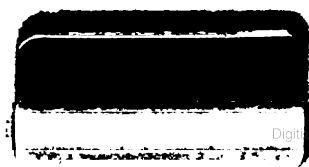
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*The principles
of electro-deposition*

Samuel Field

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THE PRINCIPLES OF ELECTRO- DEPOSITION

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THE PRINCIPLES OF ELECTRO-DEPOSITION

A LABORATORY GUIDE TO ELECTRO-PLATING

BY

SAMUEL FIELD, A.R.C.Sc. (LOND.), F.C.S.

HEAD OF THE DEPARTMENT OF TECHNICAL CHEMISTRY, NORTHAMPTON POLYTECHNIC
INSTITUTE, LONDON, E.C. ; CITY AND GUILDS HONOURS MEDALLIST IN
ELECTRO-METALLURGY ; MEMBER OF THE FARADAY SOCIETY



WITH DIAGRAMS

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THE
UNIVERSITY
OF CHICAGO
PRESS

TO
T. J. BAKER, ESQ.
(MUNICIPAL TECHNICAL SCHOOL, BIRMINGHAM)

THIS VOLUME IS RESPECTFULLY DEDICATED
IN GRATEFUL REMEMBRANCE AND ACKNOWLEDGMENT
OF HIS SYMPATHY AND KINDLY HELP
DURING THE YEARS 1891-95

235534

PREFACE

THE following pages have been written with a very definite aim. They deal with principles and their application, and the book is thus a guide.

Within recent years several treatises have appeared, dealing with the more comprehensive subject of electro-metallurgy, and some attention has there been directed to the electro-deposition of metals. Our experience goes to show, however, that the art of electro-deposition is practised by many to whom a more thorough understanding of the underlying principles would seem to be desirable. In this country, facilities for acquiring such knowledge are on the increase. The study of the fundamentals is being pursued, and in specially equipped laboratories, systematic courses of instruction are being given.

While, however, such facilities are offered, they are not within the reach of many for whom they are particularly designed, and it is partly to meet this need that this volume is now issued.

Some difficulty has been experienced in deciding to what extent assumption of previous knowledge of the simple principles of chemical and electrical science might be made. An elementary knowledge of chemistry has of necessity been taken for granted, but students are strongly urged to follow systematic courses of instruction in order to more fully comprehend the matters under discussion, and to more successfully cope with the many problems which present themselves in workshop and laboratory practice.

Details of workshop practice are but briefly treated. These matters have been elaborated in other treatises.

In Chapter III the simple principles of the dynamo have been briefly dealt with. This seemed desirable. The insight thus given may serve to encourage the inquiring student to seek for wider knowledge in larger works on the subject. A similar remark might be made with regard to the analytical section. The brief treatment is intended to be suggestive, and numerous applications are required in systematic experimental work.

With regard to units of measurements, it has not been thought desirable to rigidly adopt the metric system. The time for such a step seems barely ripe. It may, however, come soon. No apology is offered for so comprehensive an appendix. It should prove useful to the practical man with limited access to technical libraries.

The author would not fail to tender his thanks to Messrs. W. Canning & Co., Messrs. S. Grauer & Co., Messrs. F. W. Becker & Co., for the use of blocks. Most of the diagrams, however, have been executed by Mr. E. B. Ware, to whom the author especially acknowledges his indebtedness and tenders his thanks.

S. F.

NORTHAMPTON POLYTECHNIC INSTITUTE,
LONDON, E.C.

January, 1911.

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THE PRINCIPLES OF ELECTRO-DEPOSITION

CHAPTER I

Voltaic Cells and Accumulators

Generation of Electric Currents.—Electric current for deposition purposes may be generated in a number of ways, viz.—

(1) By chemical action, such as occurs when zinc dissolves in sulphuric acid in most forms of **voltaic cells**.

(2) By heating the joined ends of different kinds of wires, as in the thermo-couple. A number of these couples in parallel and series constitute a **thermo-pile**.

(3) By causing closed coils of wire to rotate rapidly in a magnetic field. This is the principle of the **dynamo**.

For work on the large scale, the last method is invariably used. Where current, however, is required only on the small scale, and the power to drive a dynamo is not available, voltaic cells such as the Smee and Bunsen are used. Occasionally, also, thermo-piles have been used for generating current for plating purposes.

The Simple Voltaic Cell.—The following simple and well-known facts will serve to lead up to the principle of this method of generating electric current.

(1) Ordinary commercial zinc dissolves freely in dilute sulphuric acid, when



(2) This action does not occur if perfectly pure zinc is employed.

(3) The solution of the impure zinc can be stopped by first coating the metal with mercury, or **amalgamating** it, as it is called. The amalgamated impure metal then behaves as pure metal, and may be used in its stead, at a much-diminished cost.

(4) If, side by side with the amalgamated zinc, a plate of copper be immersed in the acid, no action takes place. Upon touching the two metals either above or below the acid, a brisk effervescence occurs, and gas is evolved at the copper. If the two plates are weighed before and after the experiment, the zinc plate is found to have lost in weight while the copper is unaltered.

(5) If the two plates are joined by a wire which is brought near to a suspended magnetic needle, the needle is deflected from its normal position, and this is at once an indication that an electric current is flowing through the wire.

(6) Similarly, if the wire is broken, and the two ends immersed in a copper sulphate solution, the wire attached to the zinc receives a deposit of copper.

The production of an electric current is therefore associated with the solution of the zinc and the evolution of hydrogen at the copper plate. If an unamalgamated impure plate is used, gas also appears at the zinc. Gas at the zinc indicates that zinc is dissolving without generating current, while gas at the copper indicates that the zinc is dissolving and producing its equivalent of electricity. (There is no necessity to venture here any theory as to why or how these things occur.)

Such simple arrangements are shown in Figs. 1 and 2.

Direction of Current.—This is not an easy problem, but it may be simply stated that it is convenient to imagine the current as flowing in one direction, viz. from the zinc *through the acid* of the cell to the copper, thence through the external circuit back to the zinc. This is indicated by the

arrow marks shown. Of the two wires dipped into the copper sulphate solution, *b* receives the deposit, while *a* is found to

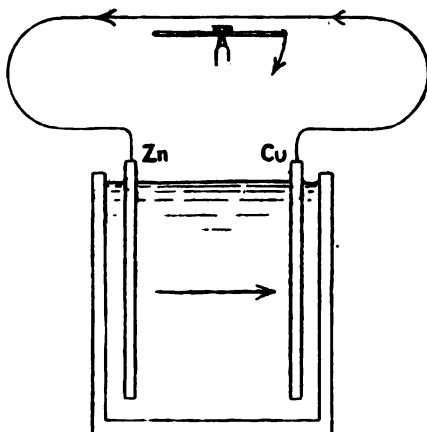


FIG. 1.—Simple cell. Deflection of magnetic needle by current.

dissolve. Thus copper seems to have been carried from *a*, through the solution to *b*, in the direction of the current. It

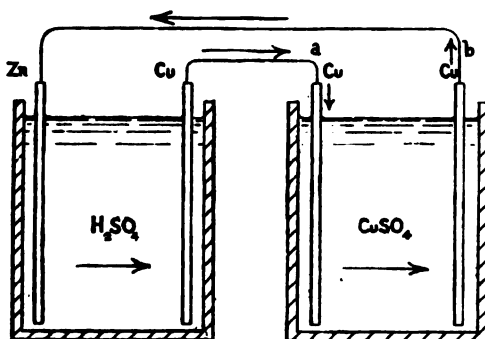


FIG. 2.—Current from simple cell depositing copper.

is therefore obvious that in using such a cell for plating purposes it will be very necessary to join up the plates correctly. The work to receive the deposit must be attached

to the wire from the zinc, and the plate serving as anode must be joined to the copper plate of the cell. The following terms are used to describe these plates :—

Zinc is the **positive plate** of the cell and forms the **negative pole**. Copper is the **negative plate** and forms the **positive pole**. This may seem confusing at first, but it is simplified if we consider electricity to always flow from positive (+) to negative (-). Thus in the previous diagrams imagine that the electricity is “made” at the zinc. It flows through the liquid from the positive plate zinc to the negative plate copper. Here it leaves the cell and flows from this positive pole (copper) back through the external circuit—resistance, vat, etc.—to the negative pole (zinc). Of the complete circuit that portion within the cell is called the **internal part**, while the remainder is known as the **external part**. *Internally*, therefore, current flows from the positive zinc *plate* to the negative copper *plate*, and *externally* from the positive copper *pole* to the negative zinc *pole*. It must not be too rigidly assumed that current flows in this one direction only. There is every reason for believing that it flows just as much in the opposite direction—that what we call current is made up of two currents in opposite directions. For our purpose it is more simple and convenient to regard the current as in one direction only.

Polarization.—In such a simple cell for producing an electric current it is found that the effect soon decreases, and may disappear altogether. This may be observed by joining up the cell to an ammeter with or without a convenient resistance. The cell soon becomes inefficient as a current producer. Its condition can then be greatly improved by shaking the copper plate, or lightly brushing it. This disengages a mass of hydrogen bubbles which have collected on the plate, and when these have disappeared the current is increased. Such increase can only be maintained by methods calculated to continually remove the gas which causes the defect. This phenomenon of decreased efficiency due to hydrogen is

called **polarization**. Hydrogen on the copper plate acts detrimentally in two ways :—

(1) Gases are poor conductors of electricity, and hydrogen on the plate therefore adds considerably to the resistance of the cell.

(2) The hydrogen *tends* to set up a current of electricity in a direction opposite to that of the main current.

We have, then, zinc sending a current in one direction, and hydrogen opposing and weakening it. This effect of the hydrogen is more readily observed when the zinc plate is

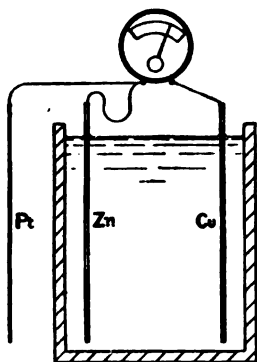


FIG. 3.—Simple cell.

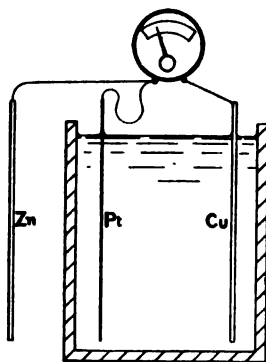


FIG. 4.—Simple cell. Zinc replaced by platinum to show polarization.

replaced by an inactive plate like platinum or carbon. The arrangement shown in Figs. 3 and 4 is convenient for this purpose, where a galvanometer—a current indicator with a needle arranged to move in opposite directions, and therefore to record opposite currents—is joined to the simple cell. When the current deflects the needle, imagine the needle to move to the right. Gradually, then, the deflection decreases, due to polarization. The zinc plate is now withdrawn without disturbing the gas on the copper plate, and a platinum plate attached to the same terminal of the galvanometer as the zinc is substituted. The needle then moves in the opposite direction.

This indicates a current in the opposite direction, not large, it is true, and, moreover, not permanent, for the hydrogen causing it is soon used up, and this current due to polarization soon decreases to zero. This polarization is the great defect of the simple cell, and must be remedied in a cell of any practical value—although, as will be seen subsequently, the phenomenon of polarization is turned to good account in that useful piece of apparatus—the accumulator. For voltaic cells we must get rid of polarization as completely as possible, and in the cells now to be described this is done by several means.

The Smee Cell is still in use in some workshops. It consists of plates of amalgamated zinc and platinized silver immersed in dilute sulphuric acid (1-10). Platinized silver is silver coated with platinum by immersing the plates in a solution of platinum chloride. The platinum deposited by the simple immersion process is not in any way corroded by the acid of the cell.

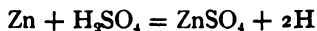
The surface of such a plate is microscopically rough, and this roughness promotes the evolution of the hydrogen, and thus reduces polarization. Whereas the bubbles of gas stick to a smooth surface, a roughened surface presents a large number of points from which the gas is easily loosened. The plate is thus kept tolerably free from gas, and the current is therefore more readily maintained. This may be regarded as a mechanical method of diminishing polarization.

The Daniell Cell was introduced in 1836, and is an attempt to eliminate polarization by causing the deposition of copper instead of hydrogen.

Figs. 5 and 6 show the construction of the cell. In Fig. 5, A is a copper vessel, at the top of which is a pocket of perforated copper. This copper pot contains a solution of copper sulphate. B is a porous cell containing dilute sulphuric acid (1-10), in which an amalgamated zinc rod stands. It is provided with a terminal screw for making the connections. The perforated copper pocket contains crystals of copper

sulphate, which must be renewed from time to time. Another form of the cell is shown in Fig. 6, where A is a glass or stone-ware tank containing the copper sulphate solution in which stands a cylinder of thin copper sheet.

In either form the chemical action is the same. Zinc dissolves in the acid thus—



The hydrogen—which is invisible—moves towards the copper,

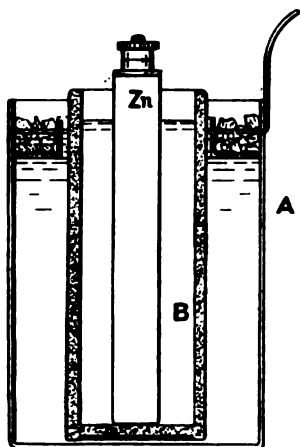


FIG. 5.—Daniell cell.

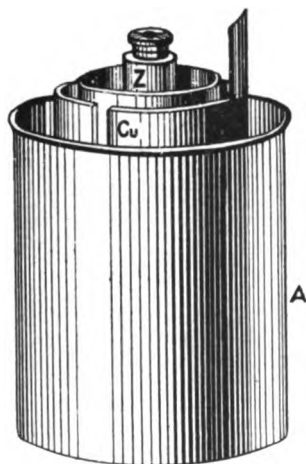
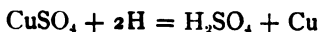


FIG. 6.—Daniell cell.
Another form.

and, passing through the pores of the cell, comes into contact with copper sulphate, from which, by a method which need not now be explained, it deposits copper upon the copper cylinder or vessel.



Copper is therefore deposited in place of hydrogen, and has the advantages of (1) offering no additional resistance to the passage of the current, and of (2) showing no tendency to develop polarization.

Obviously, the copper sulphate solution is weakened, being changed to dilute sulphuric acid. It then loses its effectiveness, and hence needs renewal by the addition of more strong solution or crystals in order to maintain its efficiency. It will be observed that the porous cell allows contact of the two liquids within its pores without freely mixing with each other. The Daniell cell gives a very constant current, and for some purposes the acid around the zinc may be replaced by a solution of zinc sulphate or even other substances.

Grove Cell.—The removal of hydrogen may also be effected by bringing it into contact with some strongly oxidizing substance like nitric acid. This is the method adopted by Grove, whose cell is depicted in Fig. 7, which shows the cell in its usual form set up. A is a rectangular glass cell, containing dilute sulphuric acid with an amalgamated zinc plate, the shape of which is shown. C is a small rectangular porous cell, containing strong nitric acid, in which is supported a piece of platinum sheet attached to a binding screw.

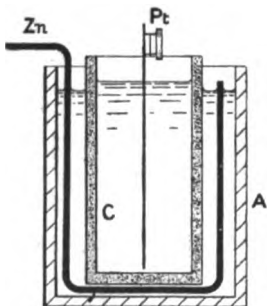
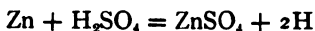
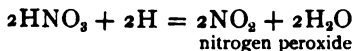


FIG. 7.—Grove cell.

When working the action is as follows:—



The hydrogen moving from the zinc passes through the porous cell, where it meets the nitric acid, when



Nitrogen peroxide is a brown gas, which dissolves in the acid producing a green colour. When the acid has become saturated with this gas, the gas is evolved, and being very objectionable, these cells should be placed in a position of good ventilation. The acid is only effective when strong, and

should not be allowed to weaken beyond a specific gravity of 1.25.

The Bunsen Cell.—The main objection to the Grove cell is its expensive platinum plate, although the platinum is not deteriorated by even prolonged action of the acid. In the Bunsen cell economy is effected by substituting for the platinum a plate or rod of gas carbon. The same acids are used though the cell takes a somewhat different shape, the zinc in the form of a cylinder surrounding the porous pot. The carbon plate or rod is cut from the hardest portion of the coke which remains in the retort in the process of gas manufacture. The ordinary form of cell is shown in Fig. 8. Cells of large capacity

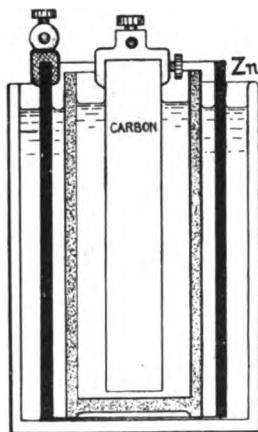


FIG. 8.—Bunsen cell.

are used in workshops where the dynamo has not yet found its way. This cell is also objectionable on account of the brown fumes evolved. It deteriorates in time owing to the reduction in the strength and consequently the depolarizing effect of the acid.

Other cells are not used much for electroplating purposes. They are not characterized by their shape, but by the chemical action occurring in them to generate the electric current.

The **Bichromate or Chromic acid** cell uses an acid solution of bichromate of potash or chromic acid as its oxidizing or depolarizing medium. The **Leclanche** cell has, as positive pole, a carbon rod surrounded by a mixture of powdered carbon and manganese dioxide (MnO_2). These materials are usually contained in a porous pot immersed in a strong solution of sal-ammoniac [ammonium chloride (NH_4Cl)]. The manganese dioxide is the solid depolarizer, and

being slower in its action than a fluid depolarizer, soon becomes ineffective and needs repose, during which it recuperates. It can thus only be used for intermittent currents, and on this account is suitable for bell work as it also needs but little attention.

E.M.F. of Voltaic Cells.—On joining up a voltaic cell to a voltmeter a definite reading is obtained for each cell when properly charged. This reading (the E.M.F.¹) is quite *independent of the size of the cell*, and is due only to the chemical action in the cell. The E.M.F.'s of the common cells are given in Table I.

TABLE I.
E.M.F.'s OF COMMON CELLS.

Cell.	E.M.F.	Cell.	E.M.F.
Simple	0·5-1·0 1·08	Bunsen	1·85
Smee		Bichromate	2·0
Daniell		Leclanche	1·5

As the materials deteriorate, however, the actions become more sluggish, polarization appears, and the E.M.F. falls off.

The current produced by cells depends upon (1) the E.M.F., (2) the internal resistance, and (3) the external resistance of the circuit. With any given external resistance the greater current will be obtained with a cell of high E.M.F. and low internal resistance. By using large plates and keeping them close together, the resistance is reduced, and as current is the quotient of electromotive force divided by resistance ($C = \frac{E}{R}$), the current is consequently increased. Where large currents are required, large cells must be used. The method in which cells should be connected for plating purposes is described in Chapter IV.

¹ E.M.F. = electromotive force (see Chapter II.).

Management of Cells.—The following points need careful attention in order to ensure effective and economic production of current in voltaic cells :—

(1) Sulphuric acid should be diluted with ten times its volume of water. Add the acid to the water, *and not the water to the acid.*

(2) Zincs should be well amalgamated, *i.e.* covered with mercury. First clean the zinc in sulphuric acid (1-6), and rub the clean surface with mercury, which will at once amalgamate with the zinc. Avoid too much mercury. The amalgamated zinc should then be free from effervescence when standing in acid (1-10).

(3) Copper sulphate for Daniell cells must be kept strong. Frequent additions of crystals in the space provided should be made.

(4) Nitric acid for Bunsen cells should be of the “aqua-fortis” type without dilution. It should be thrown away when it becomes decidedly green, or may be added to the “dipping” acid.

(5) Avoid any mixture of the nitric acid in the sulphuric acid. The same applies also to copper sulphate in the Daniell cell. Both nitric acid and copper sulphate lead to excessive zinc consumption, if present in even small quantities in the sulphuric acid.

(6) Porous pots should be well soaked in water before being used ; otherwise it will take some time for the liquids to meet within the pores of the cell. After use they should stand for hours in water. If allowed to dry without this precaution, they may crack owing to crystallization of salts within the pores of the cell.

(7) To avoid mixture of liquids in the cells where a porous pot is used, always use the sulphuric acid a little higher than the nitric in the Bunsen or the sulphate of copper in the Daniell. This prevents the nitric acid or copper sulphate from diffusing through to the zinc.

(8) Binding screws should be frequently cleaned by

dipping through nitric acid, rinsing in water and thoroughly drying.

(9) After using, zincs should at once be removed from the cell, rinsed, and allowed to dry.

The accumulator has become of great importance in workshops lately, and is a necessary adjunct to the generating plant, especially where deposition is required over long periods. Thus accumulators may be charged from the dynamo during the daytime when the full current from the machine is not being used, and when the dynamo is not running at night the

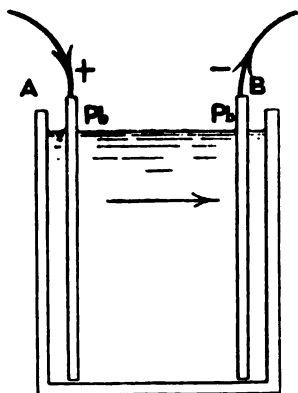


FIG. 9.—Lead plates in sulphuric acid.

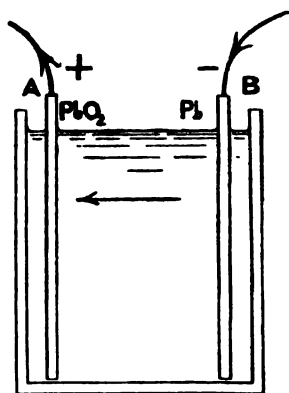


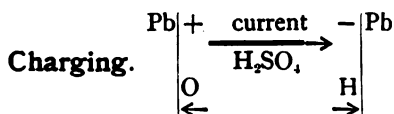
FIG. 10.—Simple accumulator. Discharging.

accumulators are switched on to the baths. With accumulators of proper capacity, baths can be kept in use continually.

Simple Principle.—It has been shown that polarization in a simple cell is a condition to be avoided, as it reduces the effectiveness of the cell. Similar polarization occurs when a current is passed through dilute sulphuric acid with platinum plates. The accumulator aims entirely at polarization, and storing it up for a time gives out a large current of polarization. If two lead plates (Fig. 9), A and B, are dipped in weak sulphuric acid, and a current passed from A \rightarrow B, then hydrogen

is given off at B and oxygen at A. The oxygen, however, partly oxidizes the lead plate, forming a brown stain upon it, this being lead peroxide (PbO_2). The cell is now **polarized**. On cutting off the current and testing the lead plates with a voltmeter, a reading of about 2 volts is obtained. This is the **E.M.F.** of polarization. From this combination (Fig. 10) current can be obtained as from a simple cell, but only for a short time. Its direction can be found by sending it through copper sulphate, and is found to be from $B \rightarrow A$.

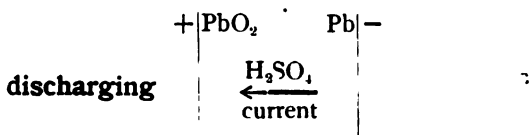
Here, then, is a simple accumulator, and all that is needed is to increase its capacity, so that by longer charging it may produce more current. The process of producing the polarization is called **charging**, while that of utilizing polarization is called **discharging**. If these two processes are alternated for a considerable time, it is found that the effectiveness of the lead plates is being increased. During these processes the following chemical changes occur :—



Then



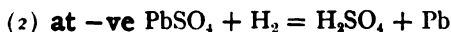
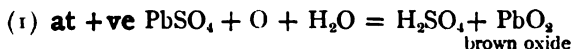
There is much doubt as to the manner in which these changes take place, but the final effects are of the greatest importance to us. Only a small portion of the oxygen produces lead peroxide. Then on—



Both plates then hold lead sulphate, and when PbO_2 has

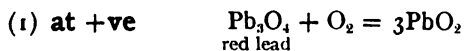
disappeared from the positive, no more current is obtainable. It will be noticed that though the direction of the current is reversed the plates do not alter their sign. The positive plate which receives the coating of peroxide is positive on charging, as it serves as anode in a cell absorbing energy. On discharging, it is like the copper in a simple or Daniell cell, the pole at which the current leaves the cell and enters the external circuit.

Now, after discharging, both plates contain PbSO_4 . On further charging we have—



The cell is then charged, and charging liberates sulphuric acid, and some idea of the extent of the charging process may be gathered from the specific gravity of the acid. Repeated charging and discharging increases the amount of "active" material, that is, the amount of lead and lead peroxide formed, and the effectiveness or efficiency is thereby increased.

This continued alternation of charging and discharging is called **forming**, and it was by this method that the capacity of accumulator was first obtained. The process, however, was long, and in order to shorten it the plates were charged with mixtures of oxides of lead, the positive with a mixture of red lead and sulphuric acid, and the negative with litharge and acid. Such plates are said to be **pasted**, and a single charging operation serves at once to produce a large amount of active material, thus—



The reactions are not so simple as would appear from these equations, but these are in essence the changes which occur. With such pasted plates, while a single charge would appear

to be sufficient, practice demands a very long initial charge, or preferably several charges with alternate discharging. From what has been said, it will be apparent that the accumulator does not accumulate electricity at all. The electrical energy put into the cell is converted into the chemical energy of the materials formed, and when these compounds again react, as they do on discharging, they throw off this energy in the electrical form. The accumulator is thus a double transformer of energy.

Construction of Accumulators.—The principles thus

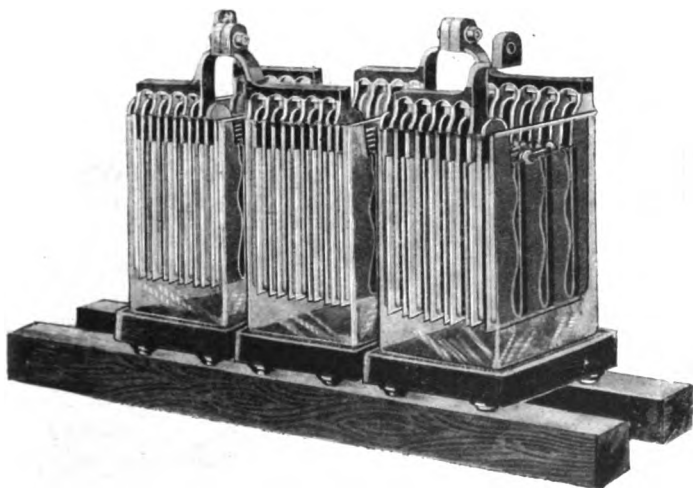


FIG. 11.—Set of large accumulators.

briefly dealt with find application in the production of cells of large capacity. Without entering into detail it may be stated that the industrial accumulator combines a large number of points which make for effectiveness and durability. Instead of two single lead plates, large numbers are put together in parallel, being of large area and placed close to one another, thus increasing the effective surface in a cell, and considerably lowering the resistance. These plates consist of lead grids charged under pressure with the pastes, so that the

active material is firmly held in little pockets in the plates. Often the negative plates are constructed of a large number of ribbons welded together at the ends. In some plates pellets of active material are firmly held in holes stamped out for that purpose. Everything is done that can be done to increase the amount of active material and its adhesion to the plate. To prevent the plates from short-circuiting they are separated by glass rods or tubes or vulcanite strips. The plates are mounted

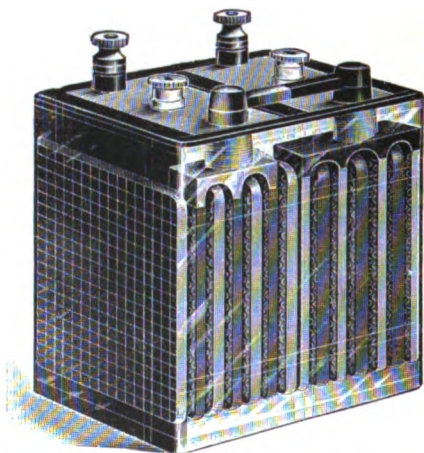


FIG. 12.—Portable accumulator.

on a wooden stand above the bottom of the cell (usually of glass), so that any active material falling from the plates shall not join two opposite plates and so at once discharge the cell. The glass cells stand in wooden trays mounted on glass insulators. Fig. 11 shows three accumulators as usually erected, while a portable form is shown in Fig. 12.

As the cells give approximately 2 volts each, only a few are required for electroplating purposes, three or four supplying more than enough E.M.F. for "striking" nickel. They should, however, be of large capacity. Accumulators lend themselves readily to the arrangement described on p. 65, where different voltages are obtainable around the workshop. Thus with four accumulators voltages of 2, 4, 6, and 8 are possible.

Management of Accumulators.—A new cell of any size has first to be erected, each part being carefully and securely placed into position. The acid should be especially pure, manufactured from brimstone, and have a sp. gr. of 1.20.

Before adding the acid the cells are placed in a circuit of suitable voltage and variable resistance; the acid is then added, and charging commenced at once. Each cell has its normal charging rate marked on the accompanying instructions, and these should be most implicitly followed. A long initial charge is usual. As the charging proceeds it will be found that a higher voltage is required to maintain the normal charging current. This alteration is effected by varying the shunt resistance of the machine, or diminishing the external resistance. Toward the end of the charge the E.M.F. required will be from 2.5-2.6 volts per cell, and this must be available from the first. Hence for four accumulators the dynamo should give from 10-11 volts. At the end of the charge the positive plate will have assumed a rich brown colour, and the sp. gr. of the acid should then be about 1.21. Further, a general milkiness of the acid and free evolution of gas accompany the end of the charging process. This initial charge should be of 12 to 24 hours. The cells are now ready for use, and on standing for a short time after charging may show 2.2 volts, which after a little discharge falls to 2.05. During discharge a number of points should be most carefully attended to. The maximum discharge rate should not be exceeded. Current should be withdrawn steadily and not suddenly. Sudden big discharges are usually disastrous to the life of the accumulator. The falling off of the E.M.F. during a normal discharge is shown in the accompanying curve (Fig. 13). Do not continue the discharge after the E.M.F. has fallen below 1.85,¹ and on no account allow the cell to stand for any length of time discharged. If cells are not required for use at once, they should be left fully charged, and further charges given periodically, for they deteriorate on standing by local action on both plates. Most carefully guard against impurities getting into the cell. These, especially metallic compounds are highly detrimental even when present in only small quantity. Examine the cells

¹ This reading being taken while the cell is sending current.

frequently with a voltmeter, and disconnect any that should, through unknown cause, be defective. After remedying the defect, either charge such a cell singly, or, according to convenience and discretion, reserve it without further use until the remainder are ready for charging. As occasion may require,



FIG. 13.—Discharge curve of accumulator.

make good any loss of liquid by evaporation, with distilled water. Special hydrometers are constructed for finding the specific gravity of accumulator acid, one of which is shown on p. 163. The acid should range between 1.17 when fully discharged to 1.21 when charged. In all cases regular working is to be preferred to irregular working.

CHAPTER II

Properties of Electric Current

HAVING now described several methods by which the electric current is generated, we pass to a consideration of some of its chief properties and characteristics. Such knowledge is necessary, having in view its correct manipulation and economical use, its distribution, control, measurement, and application in the decomposition of the plating solutions.

Effects of Electric Current in a Wire.—A wire conveying electric current possesses some striking properties. In some cases the wire may become warm or be heated even to its melting point. In any case it exerts an influence outside itself, and this is seen by bringing a magnetic needle into its vicinity. The effect in deflecting the needle and the application of this effect in the construction of measuring instruments is dealt with in Chapter VII.

Flow of Water through a Pipe.—We need here to get some simple conception, and as accurate an one as possible, of what is actually occurring in the wire. In doing this we may gain considerable assistance by considering the flow of water through a pipe, and many interesting parallels are to be observed, together with some striking differences. Omitting many preliminary steps, and remembering the well-known law that water flows from higher to lower levels, or from points of higher to lower pressure, consider what is happening when water flows through a pipe shown in Fig. 14. The pipe is marked ACDEB, and the water may be passed through it from the tap, where it is under some

pressure. The tubes I., II., and III. are connected as shown. These may be of glass, attached by means of 3-way rubber connections. Now, when water is passed through AB in the direction shown it is found to assume stationary levels in the tubes I., II., III., these levels differing in the manner indicated. Thus in I., nearest the water supply, there is the highest level, while the lowest level is obtained in III., the tube farthest from the water supply. These columns of liquid are supported by the pressure of the water at the points C, D, and E, the

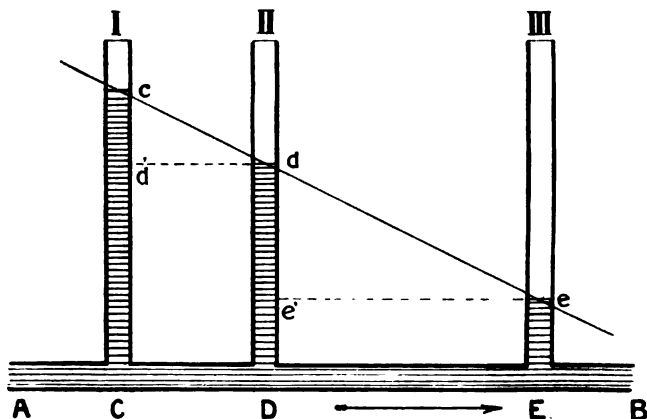


FIG. 14.—Flow of water through tube of uniform bore.

highest level indicating the highest pressure. Hence the pressure of the flowing water is gradually diminishing—there is a loss of pressure in the direction of flow. This difference of pressure is quantitatively expressed by the differences in the heights of the successive columns of water. Thus the difference of the pressures at C and D is represented by the weight (or pressure) of the water in I, above the level d' . Similarly the difference of pressure between D and E is shown by the column of water marked de' . It will be seen that even in such a simple apparatus the pressures and differences of pressure may be readily determined and expressed as pounds

per square inch, when it is remembered that a column of water 34 feet high exerts a pressure of $14\frac{1}{2}$ pounds per square inch. Now, this loss of pressure is caused by the resistance of the pipe. The greatest resistance is offered by the narrowest pipe, and the smaller the diameter of the pipe, the greater will be the differences in the levels in I., II., and III. Next, if the pipe AB is of uniform bore, then the levels in the tubes I., II., and III. lie on a straight line as shown. This occurs even if the tubes are not equidistant from each other. There is

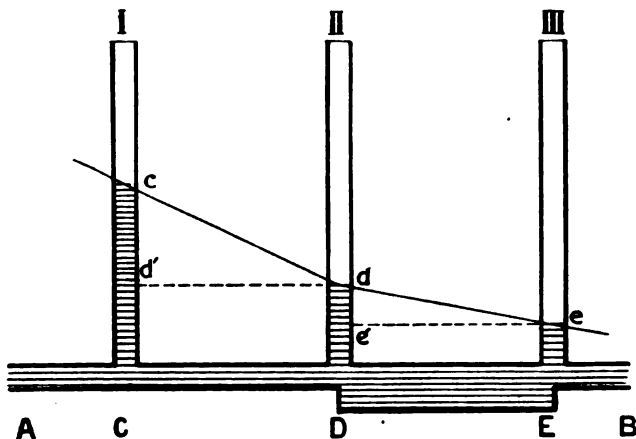


FIG. 15.—Flow of water in tube of varying bore.

uniform resistance in such a pipe, and hence this steady or uniform fall of pressure occurs. To put it in other words, as the rate of flow of water (measured, say, in gallons per hour) is—must be—the same in all parts of the pipe, the pressure required to maintain it is proportional to the resistance. Again, in Fig. 15, if the portion of the pipe marked DE is wider than CD, though of the same length, then it more easily allows the water to flow, or it offers less resistance. To overcome this smaller resistance a less difference of pressure is required, and this is shown in the diagram, where the levels do not now lie on a straight line.

In Fig. 16 a similar arrangement of pipes is shown, the circulation of the water being maintained by means of a pump.

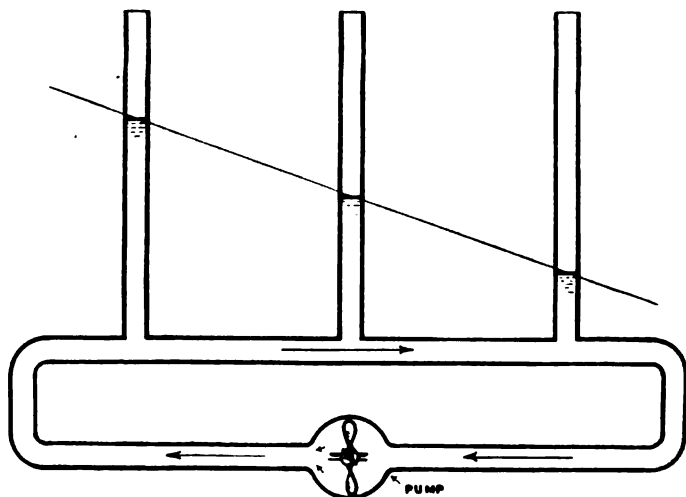


FIG. 16.—Flow of water maintained by pump.

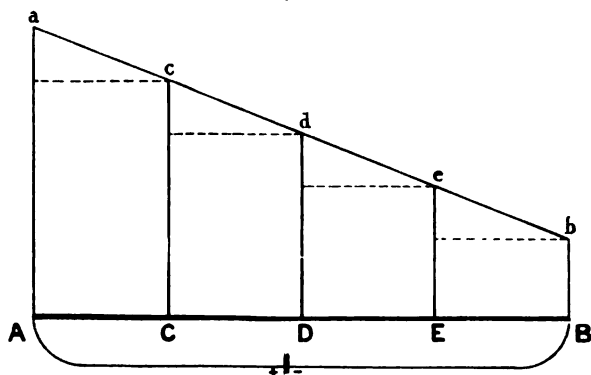


FIG. 17.—Fall of potential along a conductor.

Flow of Electricity in a Wire.—Picture now the wire AB (Fig. 17) conducting a current, as we usually say—some-what incorrectly. Electricity (similar to water) is being moved

along the wire. We measure the water in pounds or gallons. Similarly we measure the electricity in **Coulombs**, and we may define this coulomb as the **quantity** of electricity which is required to deposit 0.001118 gram silver, 0.000328 gram copper, or 0.00001035 gram hydrogen. We measure the rate of flow of water as pounds or gallons per hour—the quantity which passes in a given time. Similarly, we express the **rate of flow** of electricity as coulombs per second, minute, or hour. The rate of flow of electricity is called **Current**, and is measured as the number of coulombs per second passing any point in the wire or circuit. When the rate of flow is such that one coulomb passes a given point per second, the current is one **ampere**. We can therefore measure current by allowing it to deposit copper or silver. Thus, if in 30 minutes 1.5 grams of copper are deposited, the average current will be found thus—

$0.000328 \text{ gram Cu.} \equiv 1 \text{ coulomb}$

$$I \quad " \quad " \quad \equiv \frac{I}{0.000328} \text{ coulombs}$$

$$1.5 \quad " \quad " \quad \equiv \frac{1.5}{0.000328} = 4580 \text{ coulombs}$$

Hence 4580 coulombs have passed through in 30 minutes = 1800 seconds.

$$\therefore C \text{ (amperes)} = \frac{\text{coulombs}}{\text{seconds}} = \frac{4580}{1800} = 2.54$$

This simple idea of current being the rate at which electricity flows in the circuit should be fully grasped.

Potential—Difference of Potential and Electromotive Force.—Now, in Fig. 14 the water only moves because there is a difference of pressure between the points C and E. Similarly, in Fig. 17, electricity flows from A to B because there is a difference of pressure between these two points. In the case of electricity we call this pressure

¹ \equiv means "equivalent to."

Potential, the difference between that of any two points being the **Difference of Potential** or **Potential Difference** or **P.D.** How is this P.D. produced? In the case of the water it is the force behind the water—the pressure under which the water leaves the tap or cistern—as the case may be. In the case of electricity the force is produced by a voltaic cell, dynamo, or other means. This force is called **Electromotive Force** (the force that moves electricity), and is represented as E.M.F. Then, in Fig. 17, there are differences of potential between every successive pair of points in the whole of the circuit, and all these P.D.'s added together are equal to the E.M.F. of the cell producing the current. Again, in the case of a voltaic cell, it has a characteristic E.M.F. When the cell is standing properly charged ready to send a current there is a P.D. between its two poles. This P.D. is equal to the E.M.F. of the cell. As soon as the cell is used to produce current its E.M.F. is still the same, but the P.D. between its poles is now less, and is that part of the E.M.F. which is used in overcoming the resistance of the external circuit.

The Volt is the unit of electromotive force, and is similarly the unit of P.D. We may simply define it as that E.M.F. which produces unit current (the ampere) in unit resistance (the ohm). The **ohm** is more carefully defined in Chapter VI. as the resistance of a column of mercury 106.3 cms. long with 1 sq. mm. cross-section at a temperature of 0° C. Thus the E.M.F. of a Daniell cell is 1.08 volts, which means that if a resistance is placed between the terminals of the cell so that it makes with the resistance of the cell exactly one ohm, then a current of 1.08 amperes will be flowing in the circuit produced. We similarly speak of a P.D. of two points of so many volts, meaning that part of the total E.M.F. which is being absorbed or used between those points.

Ohm's Law.—These three units of E.M.F., current, and resistance have not been selected in a haphazard fashion.

Professor Ohm, in 1827, showed that if between any two points on a conductor the P.D. be varied, the current varies in the same manner, that is, twice the P.D. produces twice the current, or,

$$\frac{\text{P.D.}}{\text{current}} = \text{constant quantity.}$$

This constant quantity is the resistance between the two points. It only remained to select convenient units in order that this law could be simply expressed. Hence the selection of the units defined above, and, by adopting these units, Ohm's Law can be simply expressed as follows:—

(1) *For a part of a circuit—*

$$\text{Current (amperes)} = \frac{\text{P.D. (volts)}}{\text{resistance (ohms)}}$$

(2) *For a complete circuit—*

$$\text{Current (amperes)} = \frac{\text{E.M.F. (volts)}}{\text{resistance (ohms)}}$$

This simple law should be thoroughly understood, for it is the basis of a large amount of electrical measurement.

Examples of Ohm's Law.—(1) The P.D. between the ends of a resistance of 2.5 ohms is 3.6 volts. Calculate current.

$$C \text{ (amperes)} = \frac{\text{P.D. (volts)}}{\text{resistance (ohms)}} = \frac{3.6}{2.5} = 1.44$$

(2) A current of 5 amperes is flowing through a resistance of 4 ohms. What must be the P.D. between the ends of the resistance?

$$C \text{ (amperes)} = \frac{\text{P.D. (volts)}}{R \text{ (ohms)}}$$

$$\therefore \text{P.D. (volts)} = C \text{ (amperes)} \times R \text{ (ohms)}$$

$$\therefore \text{P.D.} = 5 \times 4 = 20 \text{ volts.}$$

(3) A bunsen cell of 1.85 volts is producing a current of

10 amperes. What must be the resistance of the whole circuit?

$$C \text{ (amperes)} = \frac{\text{E.M.F. (volts)}}{R \text{ (ohms)}}$$

$$\therefore R = \frac{\text{E.M.F.}}{C} = \frac{1.85}{10} = 0.185 \text{ ohm}$$

Many other examples might be given, but these are thought sufficient for the present purpose.

Use of Ohm's Law in Measuring Resistance.—

Let A.B. (Fig. 18) be a coil of wire of which the resistance

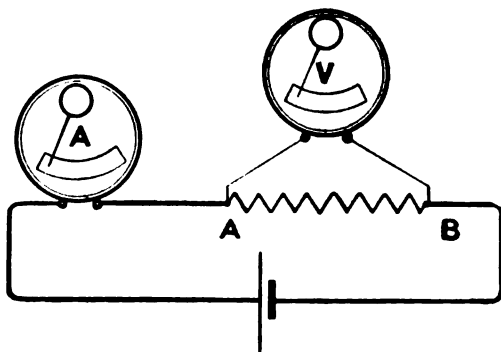


FIG. 18.—Measurement of resistance.

is required. It is joined to a source of current, say an accumulator, with an ammeter in the circuit. A voltmeter is attached across the terminals of the coil as shown. The ammeter now shows the current passing through the coil, while the voltmeter shows the P.D. between the two ends of the coil. Let the current be 2 amperes and the P.D. be 3.64 volts. Then—

$$C = \frac{\text{P.D.}}{R} \text{ or } R = \frac{\text{P.D.}}{C} = \frac{3.64}{2} = 1.82 \text{ ohms}$$

Exactly this same method would be applied to the

determination of the resistance of a bath in an approximate way,¹ and the knowledge gained is of prime importance when a solution is not behaving normally.

Electrical Work.—When a metal is being deposited from a plating solution work is being done inside the bath, and the amount of work done must surely vary with varying conditions, and be capable of quantitative expression and measurement. It will be obvious that in a number of vats with large current, more work is being done than in a single cell of small size. Without deducing every step, the following brief statements summarize the matter. Electrical work is measured in **Joules**. Mechanical work is measured in **Foot-pounds**. A foot-pound is the amount of work done in raising a one-pound weight through one foot, therefore—

$$\text{Weight (pounds)} \times \text{height (feet)} = \text{foot-pounds.}$$

One joule is the amount of work done when one ampere is produced by one volt for one second. Suppose a vat is absorbing 100 amperes at 4 volts. Every second there are $100 \times 4 = 400$ joules of work done. **Now, 1 joule = 0.7372 foot-pound (about $\frac{3}{4}$).** Hence the amount of work done in any vat in a given time can be easily calculated thus—

$$\text{Joules} = \text{volts} \times \text{amperes} \times \text{seconds}$$

and

$$\text{Foot-pounds} = \text{joules} \times 0.7372$$

$$,, \quad = \text{volts} \times \text{amperes} \times \text{seconds} \times 0.7372$$

The foot-pounds of work done in a vat when a current of 50 amperes flows under a P.D. of 2 volts for one hour

$$= 2 \times 50 \times 3600 \times 0.7372 = 265,400$$

The joule and foot-pound are, however, too small for common

¹ Assuming no polarization.

use, and larger units are therefore chosen. These will be given shortly.

Rate of doing Work.—The capacity of an engine, or the rate at which it will do work, is expressed in terms of the **Horse-power (H.P.)**.

$$\begin{aligned}\text{One horse-power (H.P.)} &= 33,000 \text{ foot-pounds per minute} \\ &= 550 \text{ foot-pounds per second.}\end{aligned}$$

Notice the rate of doing work includes two ideas, the **amount** of work done and the **time** in which it is done. Thus if 100,000 foot-pounds of work are done in 20 minutes, then this is equal to—

$$\begin{aligned}\frac{100,000}{20} &= 5000 \text{ foot-pounds per minute} \\ &= \frac{5000}{33,000} = 0.152 \text{ H.P.}\end{aligned}$$

Similarly the unit rate of doing electrical work is called the **watt**, which is equal to **1 joule per second**.

$$\begin{aligned}\text{Hence} \quad \text{watts} &= \frac{\text{joules}}{\text{seconds}} \\ &= \frac{\text{volts} \times \text{amperes} \times \text{seconds}}{\text{seconds}} \\ \therefore \text{watts} &= \text{volts} \times \text{amperes}\end{aligned}$$

But, according to Ohm's Law—

$$\begin{aligned}\text{volts} &= \text{amperes} \times \text{ohms} \\ &= C \times R \\ \therefore \text{watts} &= C \times R \times C = C^2 R\end{aligned}$$

Further, as the quantity of work done

$$\begin{aligned}&= \text{rate} \times \text{time} \\ \text{joules} &= \text{watts} \times \text{seconds or watt-seconds} \\ J_s &= C^2 R t\end{aligned}$$

where

C = amperes

R = ohms

t = seconds

The watt, however, is a small unit, and a larger one is desirable. The larger unit chosen is the **electrical horse-power** (E.H.P.), and it is the equivalent of the ordinary horse-power. Its value in watts is obtained as follows:—

$$\begin{aligned} 1 \text{ H.P.} &= 33,000 \text{ foot-pounds per minute} \\ &= 550 \text{ foot-pounds per second} \end{aligned}$$

$$\begin{aligned} \text{Now, } 1 \text{ watt} &= 1 \text{ joule per second} \\ &= 0.7372 \text{ foot-pound per second} \end{aligned}$$

$$\text{Hence } 0.7372 \text{ foot-pound per second} = 1 \text{ watt}$$

$$1 \text{ foot-pound per second} = \frac{1}{0.7372} \text{ watt}$$

$$\begin{aligned} 1 \text{ H.P.} &= 550 \text{ foot-pounds per second} = \frac{550}{0.7372} \text{ watts} \\ &= 746 \end{aligned}$$

$$\therefore 1 \text{ E.H.P.} = 746 \text{ watts}$$

and

$$\text{E.H.P.} = \frac{\text{volts} \times \text{amperes}}{746}$$

It will be obvious, therefore, that before we can estimate the size of the machine to generate the current for the plating workshop, some fair idea of the work to be done in the vats must be obtained.

The rate at which an electrical machine does work is sometimes expressed in terms of **Kilowatts**.

$$1 \text{ kilowatt} = 1000 \text{ watts}$$

$$\therefore 1 \text{ kilowatt} = \frac{1000}{746} = 1\frac{1}{3} \text{ E.H.P. (approx.)}$$

We can now consider the larger units of actual work. The joule is too small for practical purposes. Two larger units are in common use, viz. the **Horse-power hour** and the **Kilowatt hour**

$$\begin{aligned} 1 \text{ E.H.P.-hour} &= 746 \text{ watt-hours} \\ &= 746 \times 3600 \text{ watt-seconds} \\ &= 2,685,600 \text{ joules} \end{aligned}$$

$$\begin{aligned}
 1 \text{ Kilowatt-hour} &= 1000 \text{ watt-hours} \\
 &= 1000 \times 3600 \text{ watt-seconds} \\
 &= 3,600,000 \text{ joules}
 \end{aligned}$$

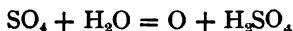
This latter unit—the kilowatt-hour—is the one adopted by the Electricity Supply Companies, and is known as the **Board of Trade Unit** (B.T.U.).

Electrolysis.

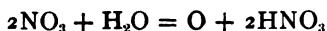
Definitions.—When an electric current is passed through a solution of a metallic salt, decomposition occurs usually with the precipitation of the metal. Such decomposition is called **electrolysis**, meaning, electro-analysis. The substance decomposed is called an **electrolyte**, though the term is usually applied also to the solution as a whole. Electrolysis is attended by the formation of two primary products called **ions**. A feature of electrolysis is that these ions move or migrate in definite directions. Those moving toward the **anode** or plate by which the current enters the solution are called **anions**, while those migrating to the **cathode** (the plate by which the current leaves the solution) are called **cathions** or **cations**. These ions do not exist under all circumstances. As soon as they reach the electrodes they become changed. Ions are electrified atoms or group of atoms. On reaching the electrodes they lose their electric charges, and are either deposited, as, for example, the metals, or enter into further chemical changes. Anions are negatively charged, and therefore move towards the positive pole. Cations are positively charged and therefore migrate to the negative pole. Sometimes when the electric charges are lost, other chemical actions occur. A simple case will make this clear.

A solution of copper sulphate is electrolyzed with platinum electrodes. At once there is an orderly movement of positively charged copper ions to the cathode, and of negatively charged SO_4 ions to the anode. The copper ions at the cathode part with their electric charges and are deposited as

metallic copper. The SO_4 ions deliver up their negative charges to the anode and then at once enter into other changes, for SO_4 has never yet been collected and preserved. In its stead, oxygen is evolved and sulphuric acid is formed, apparently thus—



While the ions are **primary** products of electrolysis, oxygen and sulphuric acid are **secondary** products. Similarly with nitrate of silver. Ag and NO_3 are the positive and negative ions respectively, and when NO_3 reaches the anode it reacts upon water, producing oxygen and nitric acid as secondary products—



Similar reactions occur with most metallic compounds, and constitute the foundation facts of electrolysis and electro-deposition.

Table II. summarizes the results from common metallic salts and a few other electrolytes : in each case with platinum electrodes.

TABLE II.

ELECTROLYTES AND THEIR PRIMARY AND SECONDARY PRODUCTS.

Electrolyte.	Products.			
	Primary.		Secondary.	
	Anion.	Cathion.	At anode.	At cathode.
Sulphuric acid H_2SO_4	} SO_4	2H {	O gas H_2SO_4	} H gas
Caustic soda NaOH	} OH	Na {	O gas H_2O	H gas NaOH
Sodium sulphate Na_2SO_4	} SO_4	2Na {	O gas H_2SO_4	H gas NaOH

TABLE II.—*continued.*

Electrolyte.	Products.			
	Primary.		Secondary.	
	Anion.	Cathion.	At anode.	At cathode.
Copper sulphate CuSO_4	} SO_4	Cu {	O gas H_2SO_4	} Cu
Stannous chloride SnCl_2	} 2Cl	Sn	Cl gas	Sn
Silver nitrate AgNO_3	} NO_3	Ag {	O gas HNO_3	} Ag
Nickel sulphate NiSO_4	} SO_4	Ni {	O gas H_2SO_4	} Ni
Copper potassium cyanide CuCN.KCN.	} Cu(CN)_2	K	CuCN {	Cu KCN

Anodes, soluble and insoluble.—If, however, copper sulphate is used with a copper anode, a different action occurs. While Cu is deposited at the cathode, SO_4 , reaching the anode, attacks the copper and forms copper sulphate. The copper compound is therefore formed as fast as it is decomposed, and thus while copper is being deposited, the amount of sulphate in the solution remains unchanged. This is a very desirable condition for continuous deposition. If the anode is not corroded to the same extent as metal is being deposited, then the solution loses metal, and difficulty is soon experienced in maintaining a good deposit of the metal. The actions at the anode are therefore of great importance. An anode which is corroded by the electrolytic action is said to be **soluble**, while if the anion does not attack and dissolve it, it is said to be **insoluble**.

E.M.F. required for electrolysis. All the metallic compounds possess a definite degree of stability. Some are very stable and hard to decompose. Others are less

stable and easily decomposed. To maintain continuous deposition a definite E.M.F. must be forthcoming. Thus zinc sulphate is more stable than copper sulphate, which in turn is more stable than silver nitrate. Zinc sulphate therefore requires a higher E.M.F. to effect its decomposition than copper sulphate. These remarks apply particularly when insoluble anodes are used.

With soluble anodes, where metal is dissolved as rapidly as it is deposited, there is in the aggregate no decomposition of the metallic salt. If the decomposition of the salt demands an E.M.F., then the formation of the salt should produce an E.M.F., and this is really what is happening at a soluble anode and at the zinc plate in an ordinary voltaic cell. With a perfectly soluble anode the only E.M.F. which is required is needed to overcome the electrical resistance of the solution and not to effect decomposition. Anodes, however, are seldom so soluble, and hence somewhat different E.M.F.'s are required for the different solutions, and these E.M.F.'s will be influenced also by the strength of the solutions and the presence of other conducting substances.

Change of Density of Solutions.—If a solution of copper sulphate is decomposed with a platinum anode, as it loses copper, so it decreases in density. This can be readily observed as a layer of lighter and less coloured liquid rising from the cathode to the surface of the bath. Similarly, with a soluble anode, as the metal passes into the solution the layer of liquid around the anode becomes heavier and denser in colour. It can be seen to fall from the plate to the bottom of the liquid. Electrolysis is therefore accompanied by a tendency to the separation of the liquid into more or less definite layers. This becomes most marked in continuous work, and leads to other difficulties. The heavier liquid at the bottom is a better conductor than the lighter liquid at the top. An undue proportion of the current is therefore conducted through it to that part of the cathode or work dipping into it, producing uneven deposition. This can be obviated by occasional stirring.

Polarization.—This phenomenon, which has been previously described, occurs also in plating solutions, especially when the anodes are not dissolving properly. In the nickel bath, for example, if the anode is not corroded perfectly (see Chapter VIII.) oxygen gas is evolved. This to some extent clings to the anode, and is partly responsible for a tendency to set up a current in a direction opposite to that of the main current. This tendency, **back E.M.F.**, or **E.M.F. of polarization**, can be easily seen on the voltmeter after the main current has been cut off, and can be approximately measured by means of a high resistance dead-beat voltmeter. Though not actually operative in producing a current from cathode to anode while the main current is flowing, still, it counteracts a part of the E.M.F. applied to that part of the circuit, and only the remainder is effective in overcoming resistance. Call this back E.M.F., e , the P.D. across the terminals being E . Then current is not $\frac{E}{R}$ but $\frac{E - e}{R}$ and unless such an allowance is made it is well-nigh impossible to find Ohm's law applying for electrolytic solutions. The most effective anode gives the least polarization and the best application of Ohm's law, and it occurs in the acid copper bath, though even in this case there is sufficient polarization to prevent the method from being applied to the accurate determination of the resistance of the bath. The nickel bath usually shows polarization very well. It is shown by the reading which remains for some time on a voltmeter attached to the electrodes after the main current has been cut off. If such electrodes are joined to a copper bath with a small cathode, polarization might be sufficient to cause a slight deposit of copper. The polarization is not persistent, as it is due chiefly to gas. If, however, a lead anode were used, then the oxygen at the anode would form lead peroxide, and be effectively stored up in that form in the same way as in the accumulator, and so the polarization would become more decided and persistent.

CHAPTER III

The Dynamo

Introduction.—As the dynamo forms the chief source of current used in plating workshops, some simple ideas of the manner in which electricity is generated and controlled in these machines should be understood by those who use and have charge of them. The subject is a large one, and only the briefest outline of the principles of action and construction can be entered upon here.

Effect of a Moving Coil in a Magnetic Field.—It was through Faraday's work that much light was thrown on the phenomena of magneto-electric induction. The simple properties of a magnet, with its north and south poles and its "field" or sphere of influence, are well known, and do not now call for detailed treatment. That magnetic and electric phenomena are closely related has been known for a long time. To illustrate this relation, let A (Fig. 19) be a coil of wire attached to a current detector, B; C is a bar magnet with its poles marked. If the magnet

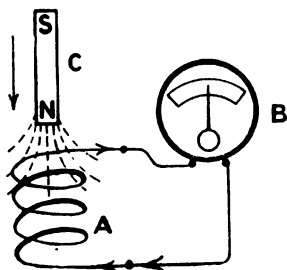


FIG. 19.—Showing direction of induced current.

is lowered into the coil a current is produced, and this is indicated by the detector, *but the current lasts only while the movement of the magnet goes on.* If the magnet is now withdrawn, a new current can be observed in the opposite

direction. These **induced currents** are due to the closed coil cutting the lines of magnetic force, and are dependent upon the rate of cutting of the lines of force for their magnitude, while their direction is governed by several conditions. Thus, if the thickened parts of the coil are in front and the magnet descends N pole first, the direction of the current is that shown by the arrows, and the direction of the current would be reversed by any one of the following changed conditions: (a) an oppositely wound coil, right-handed instead of left-handed; (b) south pole introduced first instead of north pole; and (c) the magnet moved in the reverse direction. A stronger magnet would produce a more pronounced current, and this would be increased also by a larger number of turns

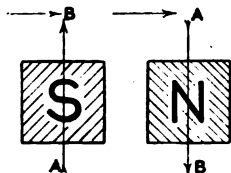


FIG. 20.—Direction of induced currents.

in the coil or a more rapid movement. The same effect can be illustrated in another way. Let S and N (Fig. 20) represent the faces of south and north poles. In each case AB is a wire which forms part of a closed circuit. It is moved from left to right, and in so doing cuts the lines of force which proceed from these poles. The direction

of the current produced in each case is indicated by the arrow marks.

Again, to come closer to dynamo conditions, let N and S in Fig. 21 represent the north and south poles of a horseshoe magnet. ABCD is a closed coil of wire rotating about the axis XY clockwise. The current generated before the coil comes into the vertical position is in the direction ABCD. The armature of a dynamo is in reality a number of such coils mounted on an iron core, the purpose of which will be afterwards explained.

Character of Current produced.—To examine this induced current the coil must be opened and attached, say, to a voltmeter, in such a way that the rotation is not interfered with. This is shown in Fig. 22, where a coil of two loops

is drawn. The ends of the coil are now attached to two copper or brass "slip" rings mounted on the spindle by an insulating material. Light copper strips, S, S, press on

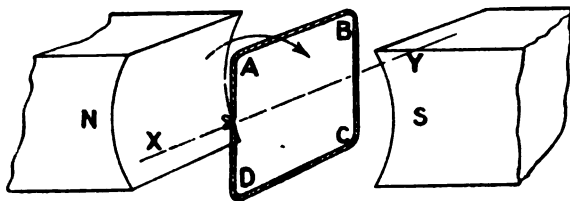


FIG. 21.—Induced current in rotating coil.

these rings and are joined to the voltmeter. Let the coil be now rotated at a uniform speed, and the E.M.F. generated in

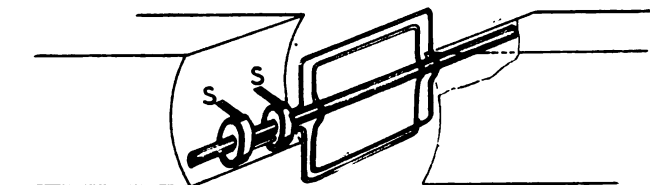
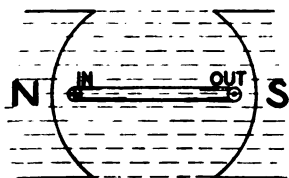
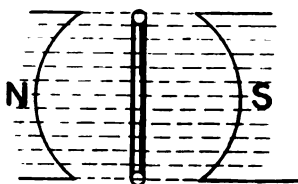


FIG. 22.—Coil with two loops and slip rings.

each position observed. The special arrangements for this purpose need not be described. *Now E.M.F. depends upon the*



A. Coil horizontal.



B. Coil vertical.

FIG. 23.

rate of cutting lines of force. Figs. 23 A and 23 B show a coil in the horizontal and vertical positions. From this diagram note the following points :—

(1) As the coil passes the vertical position it momentarily ceases to cut lines of force, and there is therefore no E.M.F.

(2) In the horizontal position there is the maximum rate of cutting lines of force, and therefore maximum E.M.F.

(3) Between the horizontal and vertical positions, the rate of cutting lines of force diminishes, and thus the E.M.F. diminishes with it.

(4) The direction of the current is shown—IN meaning into the paper, and OUT referring to the opposite direction, that is, out from the paper. These are in future represented

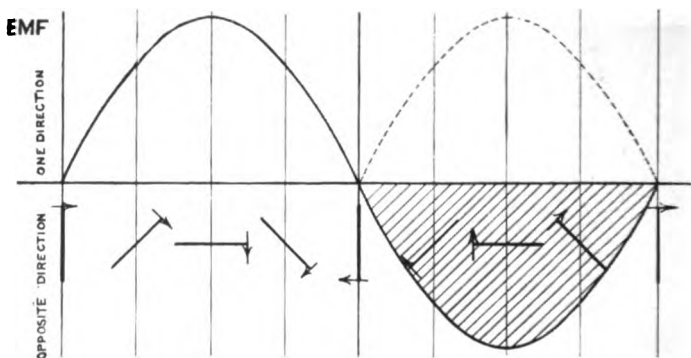


FIG. 24.—Curve of E.M.F. for one complete revolution.

as \odot and \otimes , respectively representing the end and point of an arrow moving in the direction of the current.

(5) Obviously, therefore, the current changes in direction as the coil passes the vertical position.

Plotting the E.M.F.'s produced at the different stages and also showing the corresponding positions of the coil, we get the diagram in Fig. 24 for one complete revolution. Such a current is called an **alternating current (A.C.)**, and the machine an **alternator**. It will be obvious that a current of this type will be useless for plating purposes, owing to its change of direction each half-revolution. For plating purposes current in one direction only is required. If we could only twist

the curve in Fig. 24 so that the half below the line occupied the position shown by the dotted line, the current would at least be **unidirectional**, though varying in strength during the revolution. This change is effected by a **commutator**, a simple form of which is shown in section in Fig. 25. It consists of a copper ring which is suitably mounted by an insulating medium on the shaft so that it rotates with it. This ring is divided into two quite separate segments by longitudinal cuts at opposite ends of a diameter. The copper strips which act as brushes are mounted vertically opposite to each other. The ends of the coil are attached to the segments in such a manner that when the coil passes the vertical position, when no cutting

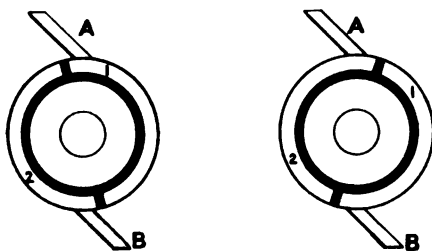


FIG. 25.—Two-part commutator.

of lines occurs, and when, therefore, there is no E.M.F. in the coil, the segments in contact with the brushes change. It will thus be seen that although the current in the coil and segments changes its direction twice in one revolution, that in the brushes and outer circuit is always in one direction, for the moment the current changes its direction in the coil, the segments change their contact from one brush to the other, thus maintaining current in one direction in the brushes and external circuit. The current now generated in the external circuit, though in one direction, is still not uniform. It is called a **pulsating** current, and in its place a steady current is required. A step in this direction can be taken by adding a quite separate coil at right angles to the first coil, and joining its ends to the alternate segments of a four-part commutator, the first coil

being joined to the other two segments (as shown in Fig. 26). It can then be arranged that the brushes shall take off the maximum current from the two coils. As the current in one is diminishing, so the brush comes into contact with another segment in which the E.M.F. is increasing. This is shown in

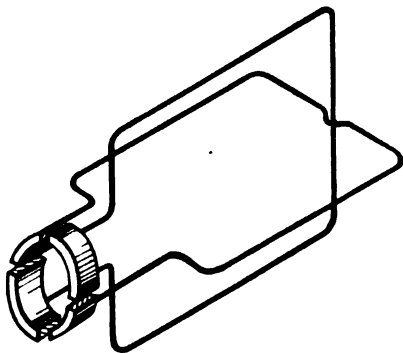


FIG. 26.—Two coils connected to a four-part commutator.

Fig. 27, the thickened curve showing the value of the E.M.F. impressed on to the external circuit. The fault of the arrangement, however, is that the E.M.F.'s generated in the coils for

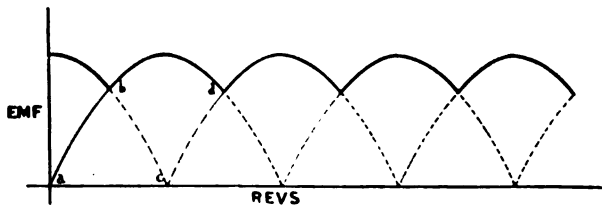


FIG. 27.—E.M.F. curve for two coils arranged as in Fig. 26.

the parts of the revolutions marked *ab*, *bc*, *cd*, etc., are not transmitted to the brushes and external circuit, but are wasted. They may be saved and utilized by a modification of the method of winding and joining to the commutator. The E.M.F. curve is then obtained by adding the two E.M.F.'s

of the separate parts of the coils, and the steadier current of higher E.M.F. is obtained. This is shown in Fig. 28. By following out this principle still further, it will be seen that by using 16 or 32 segments the pulsations will be so frequent and small as to become negligible, and a practically continuous steady current is obtained.

Effect of increasing the Number of Coils.—The E.M.F. generated in a single coil, even in a strong magnetic field, is very small, and for currents of industrial magnitude the effect must be multiplied. By increasing the number of coils in series, all the little E.M.F.'s generated in them will be added together, as they are in a battery of

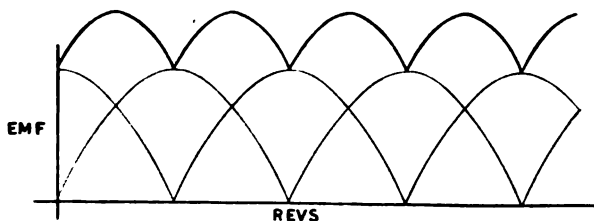


FIG. 28.—E.M.F. curve for two coils in series.

voltaic cells, and this system has therefore to be adopted in order to produce E.M.F.'s sufficient, say, for the purposes of plating or lighting, and such coils will be arranged and connected to the segments in a manner which will allow of the most economic use of all the little E.M.F.'s generated. Now, for electric lighting, a much higher E.M.F. is required than for electroplating. For the former, 100–110 volts is in common use, and frequently 200 volts, while for plating purposes, 10 volts would meet practically all requirements, and would also allow for charging four accumulators in series. For the former higher voltage, more coils will be required in series than for the latter lower voltage. Again, a plating dynamo with its low voltage is required to produce large currents. In order that the rotating coils shall have the necessary carrying

power to avoid undesirable heating and loss, additional coils must be put on in parallel. Thus a low internal resistance of the machine is also obtained, which is of the greatest importance. The resistance of a number of plating baths is compared with a number of electric lamps, very small, and the internal resistance of the machine must of necessity be considerably smaller, otherwise an undue proportion of the energy put into the machine will be wasted in overcoming this internal resistance, and thus developing unnecessary heat. For a machine to develop 200 amperes at 10 volts, the total resistance of the whole of the workshop circuit and machine must not exceed—

$$C = \frac{E}{R} \quad \therefore R = \frac{E}{C} = \frac{10}{200} = 0.05 \text{ ohm}$$

If the internal resistance of the machine is as high as 0.01 ohm, then $\frac{1}{8}$ of the E.M.F. will be required in the machine, and only $\frac{4}{8}$ will be available externally. This means that $\frac{1}{8}$ of the energy put into the machine will be wasted in the dynamo, producing heat. The necessity, therefore, for paralleling many coils in a plating dynamo is obvious. In the case of a lighting dynamo, the following simple figures show a striking contrast. A 16-c.p. carbon lamp on a 100-volt circuit has a resistance of nearly 200 ohms, and thus carries a current of half an ampere. With 200 such lamps in parallel, the external resistance would be 1 ohm, and the total current 100 amperes—a very different condition of things from that existing in the plating circuit. Further striking differences between the plating and lighting dynamo will be dealt with later.

Parts of a Dynamo.—The essential parts of a dynamo are shown in Fig. 29. F.M. represents the **field-magnet**. These are commonly of the horseshoe shape, the N and S poles being close together, the space between them being called the “air-gap.” In this gap an intense magnetic field is set up, the lines of this field being cut by the rotating coils of the armature.

in such a gap between the shaped poles, any single coil in rotation will pass through a uniform field for a larger part of each half-revolution, and the curve of E.M.F. obtained will be much flatter than that shown in Fig. 24. The field-magnets may be of other shapes, and have sometimes more than two poles. With two poles they are called **bi-polar** machines; with more than two poles, **multi-polar**. These field-magnets are made of soft iron, but this material cannot retain much

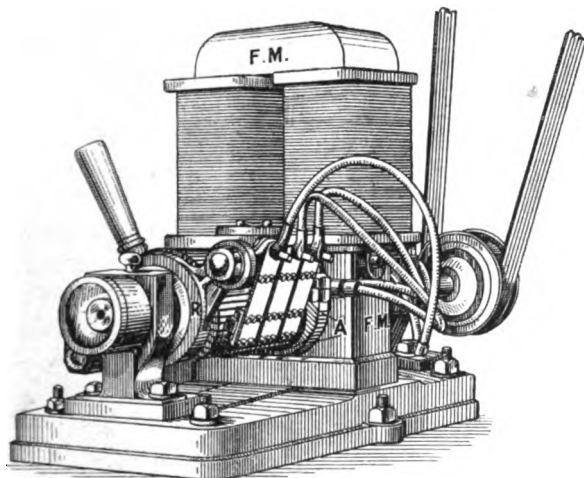


FIG. 29.—Essential parts of a dynamo.

magnetism, and there arises, therefore, the necessity of intensifying the effect. This is done by sending a current through coils of wire wound round the magnets. The magnetic effect is considerably increased, and the arrangement constitutes an **electro-magnet**. These coils are the **magnetizing coils**, the **field windings**, and the current passing through them the **exciting current**. There are different ways of exciting a field-magnet, and these will now be explained.

Field Windings.—There are four chief methods by which a dynamo may be excited, each having its special advantages and utility for special purposes.

(1) **Separate Excitation.**—The current may be supplied from an external source, either a battery or smaller machine, as shown in Fig. 30. If

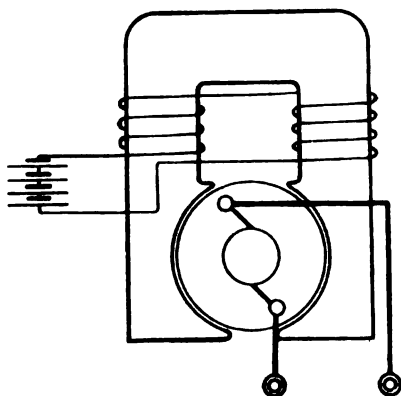


FIG. 30.—Separate excitation.

such a current is constant, a constant P.D. can be maintained at the dynamo terminals, for the magnetizing current is not affected by the variations of the current in the main circuit. Now, the behaviour of the dynamo is very dependent upon

its winding, and this is shown in what are called **characteristic curves**. Thus in

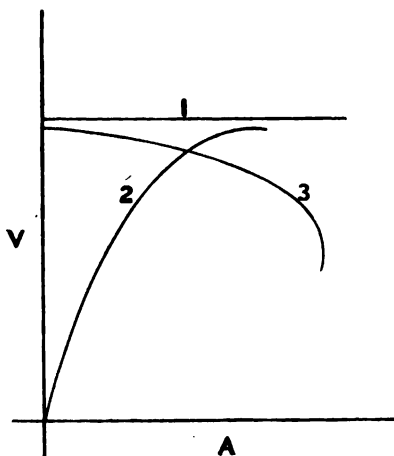


FIG. 31.—Characteristic curves.

Fig. 31, if the volts are plotted against the output in current, then for this separate excitation we get a "curve" (No. 1), which is practically a horizontal line, that is, a P.D. independent of the load on the machine. This method of excitation is only used in special cases.

(2) **Series Winding.**—In exciting a magnet by means of a coil carrying a current,

two factors chiefly determine the strength of the field produced: (1) the current in the coils, and (2) the number of turns in the

coil. The magnetic effect is proportional to the current and also to the number of turns in the coil. It is therefore proportional to the product of the two quantities, and the product of the amperes and turns is called the **ampere-turns**. To produce any required magnetic effect, if a large current is used, then only a few turns in the coil may be necessary, while if only a small current is used a proportionately larger number of turns must be present in the coil.

In the series winding (Fig. 32) the main current of the machine passes round the magnetizing coils, and whatever variation of current occurs in the outer circuit, occurs also in the magnetizing coils. This means that until there is some appreciable current in the main circuit there cannot be proper excitation, for the residual magnetism of soft iron—that is, the magnetic effect which remains after the excitation has been withdrawn—is small. Thus the full E.M.F. of the machine is not at first forthcoming. As the current increases, so does the E.M.F., and the characteristic curve obtained is shown in Fig. 31, curve 2. From the plating point of view this is a great disadvantage, but a greater one exists. Many plating baths set up a polarization which becomes apparent when the current is cut off. If a series-wound machine is slowed down while still connected to the baths, it may easily happen that the current of polarization in the reverse direction may be sufficient to reverse the polarity of the field magnets. On starting up the machine again the direction of the current will be reversed, leading to much trouble in the baths until discovered and corrected. There are thus serious

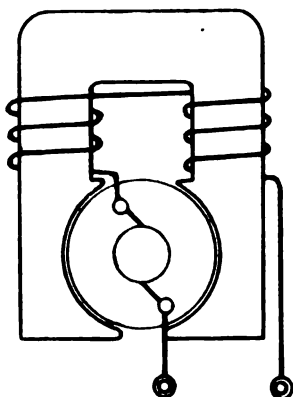


FIG. 32.—Series winding.

objections to the use of a series-wound machine for plating purposes.

(3) **Shunt Winding.**—A different method of exciting the field magnets is to use only a part of the current generated in the machine. This is the shunt system, in which the

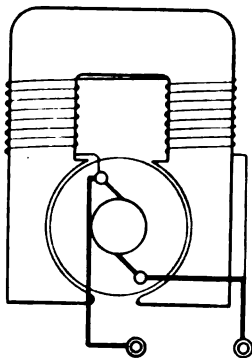


FIG. 33.—Shunt winding.

magnetizing coils are connected as a shunt across the brushes. As only a portion of the current is being used, its effect must be intensified by passing it round a larger number of turns, the magnetizing effect being proportional to the ampere-turns. This is shown in Figs. 33 and 34. The value of this system is seen in more ways than one.

(a) If through careless shutting off of the machine a current of polarization passes back to the magnetizing coils, it passes through them in the *same* direction as the original exciting current, and there is thus no chance of reverse magnetization. -

(b) The full P.D. can be obtained without any external current, for while no current is passing through the main circuit there is still a complete circuit in the magnetizing coils, and thus the full P.D. can be developed. This is of great advantage both for electroplating purposes generally and also for charging accumulators, a matter closely connected with the plating workshop.

(c) In a series machine an increase in current in the main circuit increases the effect in the field windings, and if this is carried too far a point of danger from overheating is reached. In a shunt machine, however, a greater current in the main circuit involves a slightly reduced current in the shunt winding, and this leads to a more or less automatic regulation of the E.M.F. of the machine, the characteristic curve being shown in Fig. 31, curve 3.

(d) Now this slight falling off of P.D. which is seen in the curve may be easily counteracted. A small resistance can be placed in the shunt circuit, and slight variations in this resistance alter the current in the magnetizing coils, and such means can be adopted to maintain a constant P.D. at the terminals of the machine. Such regulation is especially

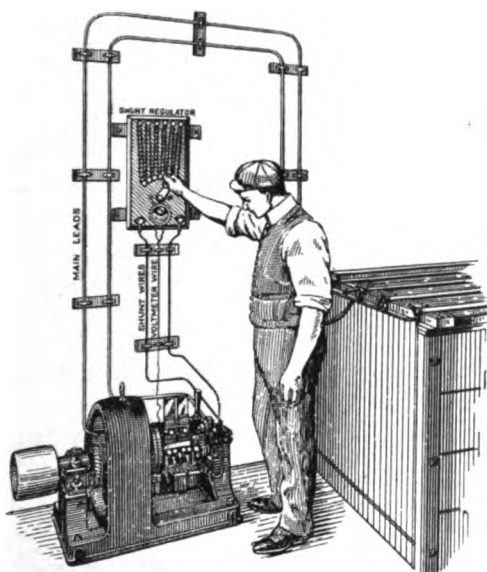


FIG. 34.—Variation of resistance in shunt winding.

advantageous in charging accumulators, when, as the charging proceeds, the increased polarization demands an increased E.M.F. up to 2.5–2.6 volts per cell to maintain the constant charging current. This shunt regulation offers advantages also to the plater, for in such a machine giving, say, 15 volts, shunt regulation may easily reduce this to 7–8 volts. Resistances, therefore, in the main circuit may be much less than those required without shunt regulation. Further, the regulation of the shunt resistance can easily be

controlled from the main switchboard in the workshop, and this arrangement is shown in the diagrams in Chapter V.

(4) **Compound Winding.**—A glance at the characteristic curves for series and shunt machines shows that in the

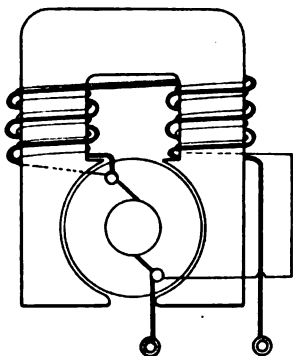


FIG. 35.—Compound winding.

one case the E.M.F. of the machine is considerably increased with load, while in the other case it suffers diminution. It should be possible, therefore, so to combine the two systems that a constant P.D. should be obtained. This is done in the winding shown in Fig. 35, the thick wire of very few turns carrying the main current, and the thin winding of many turns carrying a shunted current. This is the compound winding system—a constant P.D.

being maintained by the balance of the opposite effects of the series and shunt coils.

The Armature.—In Fig. 29 the armature is shown at A.

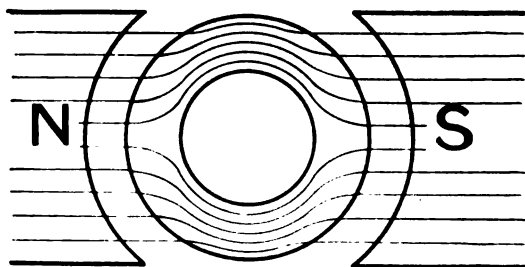


FIG. 36.—Showing magnetic lines through armature core.

This consists of an iron drum or ring on which the rotating coils are mounted. The core of the armature is made of iron, the reason for this being seen from Fig. 36, where with an iron core the lines of force passing between the poles of

the field magnet are concentrated through the more permeable or easily magnetized core, and are therefore cut in larger numbers by the coils mounted on the core. Further, when the poles are shaped with curved ends the armature nearly fills up the whole of the gap, and this produces a greater concentration of lines in the core. Armature cores are either of the **drum** or cylinder type or of the **ring** type.

Drum Armature.—With the drum armature the coils are wound on the outside of the drum, and all the wire wound

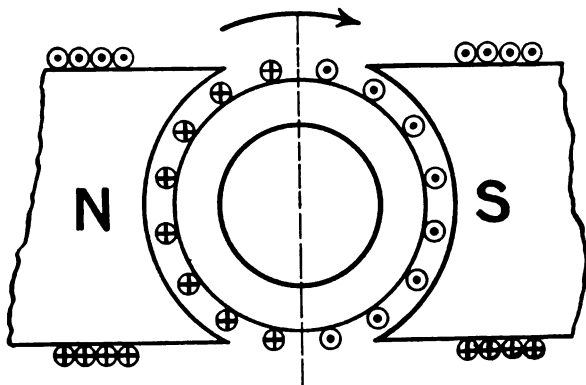


FIG. 37.—Direction of current in coils of drum armature.

upon it, except that on the ends, is actively engaged in producing E.M.F. during rotation. Such an armature is really built up of a number of these simple coils arranged in series and parallel according to the requirements of the machine.

Fig. 37 shows a number of coils on a drum armature. The direction of current in these coils is indicated in the usual manner, and also that of the current in the field windings. Such an armature is shown in Fig. 38.

A **Ring armature** is shown with a single coil wound upon it in Fig. 39. It must be observed, however, that only the parts of the coil on the outside of the ring are effective in setting up E.M.F. The inside portions do not cut lines

of force. They serve simply as connections for the outer portions. It will be interesting to observe how current is tapped from such coils on a ring armature. In Fig. 39, it will be seen that the coil is a continuous one, but is divided into a number of equal portions, in this case eight. These

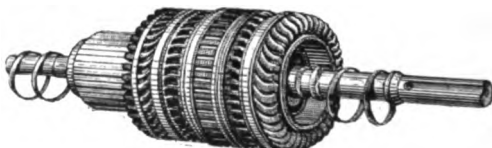


FIG. 38.—Drum armature.

eight points are connected to the segments of the eight-part commutator. Now, when the coil is rotated clockwise there is the tendency to set up currents in it in the directions indicated by the arrows. These currents, however, are in opposition. Thus, in the portion from A to B the current is clockwise, while from B to C it is anti-clockwise. Similarly from

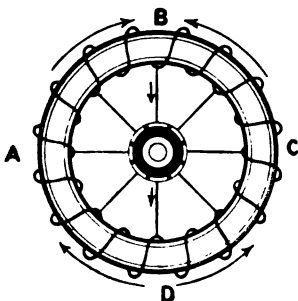


FIG. 39.—Ring armature.

C to D it is anti-clockwise, and from D to A clockwise. Consider particularly the point B in the vertical, where lines of force are not being cut. At this point there are two opposing E.M.F.'s directed to the point B, and hence raising its potential. At D there are two opposite E.M.F.'s directed away from D, and hence lowering its potential. If B and D are joined a current will flow

from B to D, and the circuit is completed between these points by the commutator, brushes, and external circuit, and the current thus produced in the main circuit is the sum of two opposite currents in the coil of the ring armature.

The two types of armature, drum, and ring have their relative advantages and disadvantages, but these need not be

entered upon here. Another point, however, may be noticed. These armature cores are not of solid metal, but are built up with a number of thin sheet stampings of the metal which have been previously varnished with shellac varnish. In some cases they are separated by layers of varnished paper. Cores built up in this fashion are said to be laminated, and the system is adopted in order to prevent the setting up of numerous small induced currents called "eddy currents." These involve loss of energy and overheating. Again, it will be seen that the energy put into the machine has to be transmitted from the armature core, which is fixed to the shaft, to the coils. When current is being induced in these coils, considerable resistance is experienced to their passage through the magnetic field. It is, in fact, the motion of these coils against this resistance which accounts for the absorption and conversion of the mechanical energy put into the machine. The transmission of this energy from a smooth core to the coils wound upon it is a matter of some difficulty, for it will be seen that sudden changes in the load will put considerable stresses on these coils, tending to tear them from the core.

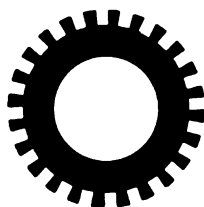


FIG. 40.—Slotted armature.

To avoid this, armature cores are often **slotted**, and the coils are then wound in the slots. A section of such an armature is shown in Fig. 40. These slots give a direct drive to the coils, and moreover allow the armature core to more completely fill the gap, and thus increase the concentration of the lines of force through the rotating coils.

The Commutator.—The function of the commutator has already been explained. By it the rapid alternations of current are grouped together according to their direction, and are marshalled together to produce a unidirectional current. It consists of a number of segments most carefully insulated from each other, to which the groups of coils are attached. It has already been shown that the greater the number of

segments the smaller will be the pulsating effect of the current. The segments are of best copper, and are built together on an insulating block. The dimensions of the commutator are controlled by the current to be transmitted, and special attention has to be directed to this point in machines for electrometallurgical work. In some large machines the commutator is divided into two parts, one at either end of the armature, so that the current can be more successfully transmitted to the brushes without undue heating.

Position of the Brushes—Lead.—In the simple explanation of the action of the dynamo it was shown that with the magnetic poles in the horizontal position, the coil rotated between them ceases to cut lines of force when it reaches the vertical position—that is, when the plane of the coil is at right angles to the magnetic field. In the case of a single coil it is at this point that commutation should take place, for at the next moment the direction of the current will be reversed. In order to effectually commute, the brush should be adjusted to meet this condition. This, however, is taking only a very simple case. A further point, which considerably affects the position of the brushes, must now be explained. The magnetic field in the gap apart from the armature is practically a straight one. The effect of the core has also been shown (Fig. 36) in producing a concentration of lines of force through the armature coils. Next, when a current is passing through the armature coils another magnetic field is set up about the coils. In Fig. 41 one coil only is shown, and the direction of the current indicated. The lines of force in air would be circular. In contact with very permeable iron, however, the lines are concentrated in the iron, both of the poles and also of the core. The magnetic field induced by the current in the armature coils is therefore of the shape shown in Fig. 41.

The total magnetic field in which the armature rotates is therefore a combination, or a resultant, of those produced by the field-magnet and the armature current. Such a resultant of imposing one field over another may be easily traced by

means of iron filings, and the direction of the lines of force is now that indicated in Fig. 42. The field is said to be twisted, and it will be seen that the neutral line AB, or the position of

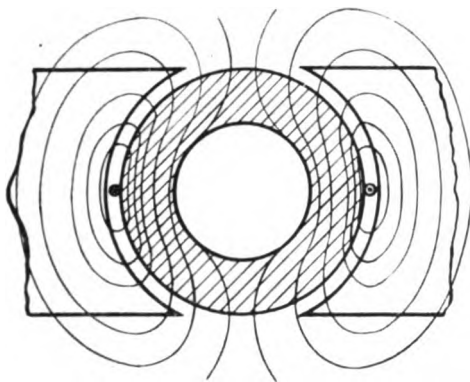


FIG. 41.—Magnetic field due to current in armature coil.

a coil when it momentarily ceases to cut lines, is moved forward in the direction of rotation of the armature. The brushes must therefore be moved forward, in order to come

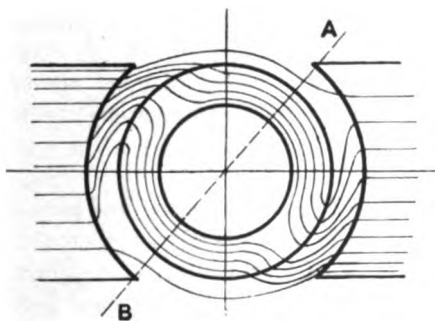


FIG. 42.—Twisted field showing advance of neutral line.

into the new position. This forward position of the brush is called the **lead**. As the output of the machine is increased, so the induced magnetic field about the armature coils is

intensified, and a further twisting of the field occurs. It will be seen, therefore, that the brushes must be advanced still further forward to find the neutral position, and, as a matter of fact, the brushes should be advanced a little beyond this position for sparkless commutation. In order to allow of the easy adjustment of the brushes to the altered conditions, they are mounted upon a **rocker** (R in Fig. 29), which in a small machine is adjusted by hand, and in a large machine is controlled by gearing.

Care and Maintenance of the Dynamo.—A few notes concerning the management of the machine may be added to conclude this section. The erection of the dynamo is a matter more for the electrical engineer. The machine, however, should be installed in a dry place, with good foundations, and in a position of good ventilation, preferably away from the workshop. If placed in the plating-room, it may be enclosed in a thin wooden case to protect it from the fumes; but it then lacks the ventilation which is so desirable to prevent undue elevation of temperature. It may be driven from any source of power at hand by suitable pulleys, arranged to give the speed for which the machine is designed. Where electric power is in use, the dynamo may be conveniently run by a motor directly coupled to it, and if the only available power is alternating current, the combination of alternating current motor and direct current generator effects the necessary change from A.C. at high voltage to D.C. at a voltage suitable for plating work.

The machine is then slowly started, and when the maximum speed has been attained the brushes are allowed to press on the commutator. If a good contact is obtained, then, in the shunt machine, the full voltage is at once forthcoming, and current may be taken from the machine, though not too suddenly. Sudden changes of current should be carefully avoided, as these throw unnecessary strain upon the armature coils. As the current in the external circuit increases, the brushes must be moved forward to the position where no

sparking occurs, and this position will need alteration with appreciable changes of load.

The commutator should be perfectly smooth and clean, and the brushes rest closely upon it. If the brushes or commutator are uneven, sparking occurs, and to remedy this the brushes should be removed and carefully trimmed. The commutator may require cleaning occasionally, owing to the collection of dust upon it, and the brushes may become clogged through the same cause. In cleaning the commutator paraffin applied with a soft rag or duster will be found effective. Oil or grease in any quantity should be avoided. Too great a pressure of the brushes will cause the commutator to wear away unduly and unevenly, besides causing a rise in temperature by unnecessary friction.

CHAPTER IV

Arrangement of Apparatus in the Circuit

Preliminary.—One of the first matters demanding the attention of an electroplater is that of arranging his plant, and the connections of his circuit are often puzzling. This is simplified when he finds dynamo and vat connections already made and the necessary instruments already in position, but to substitute a number of accumulators for the dynamo, or a number of different baths in the place of one

single vat, is a matter which can only be correctly accomplished by the right application of simple yet important principles.

Diagrammatic Representation.—In as simple a manner as possible it is desired to show the necessary connections which might be required under all ordinary conditions.

The Generator or producer of the electric current may be a dynamo or a battery of cells. The representation of a voltaic cell will serve equally well for an accumulator. In any case the generator has two important

terminals, viz. the positive (+) by which the current leaves, and the negative (−) by which the current returns to it. It may be simply represented as in Fig. 43, D, showing the commutator and two brushes.

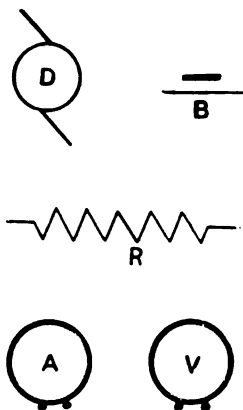


FIG. 43. — Diagrammatic representation of apparatus.

For voltaic cells the sign shown (Fig. 43, B) is in common use, the thick short stroke representing the zinc or - pole, and the thin longer stroke the + pole. Accumulators may be similarly represented. Resistances may be shown by a zigzag line, while ammeters and voltmeters are conveniently shown by circles containing A and V respectively. The vat may be represented in quite a number of different ways, of which three are shown in Fig. 44, where (a) represents one anode and one cathode, (b) two anodes and one cathode, and (c) a larger number of electrodes.

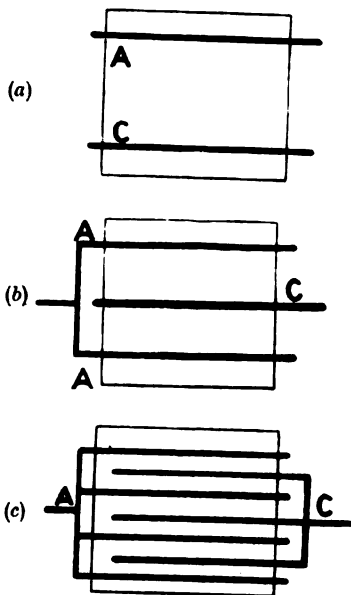


FIG. 44.—Representation of vats.

The **Simple Arrangement with dynamo** is shown in Fig. 45, on which the only remark necessary is that the order of the apparatus is immaterial so long as the anode is connected directly or indirectly with the + pole of the dynamo, and the cathode directly or indirectly to the - pole of the dynamo. Should any doubt exist as to the polarity of the machine it should be tested either by (1) wires passing from the poles and immersed in a copper sulphate solution, when the negative wire receives a

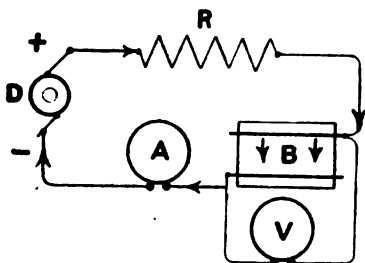
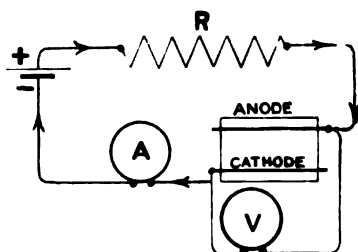


FIG. 45.—Simple arrangement of apparatus with dynamo.

deposit of copper, or (2) by using pole-paper. This may be made by soaking filter paper in a neutral solution of sodium sulphate, to which a little phenolphthalein has been added.



dry, the papers can be reserved, and for use they are moistened with water and the wires from the terminals laid on. The wire proceeding from the negative pole produces a dark stain.

FIG. 46.—Simple arrangement of apparatus with cell or accumulator.

Fig. 46 shows a similar arrangement using either a single voltaic cell or

accumulator. In each case the direction of the current is shown by arrows.

Figs. 47, 48 and 49 show clearly the arrangement of ammeter

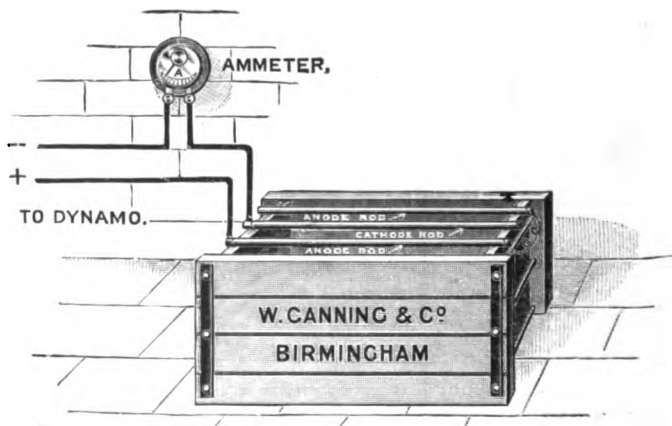


FIG. 47.—Ammeter in the circuit.

and voltmeter. The ammeter is placed directly in the circuit and measures the *total current* passing through the circuit. The voltmeter is connected as a shunt across the vat terminals,

and by means of a *very small current*, which in passing through it is diverted from the bath, registers the potential difference

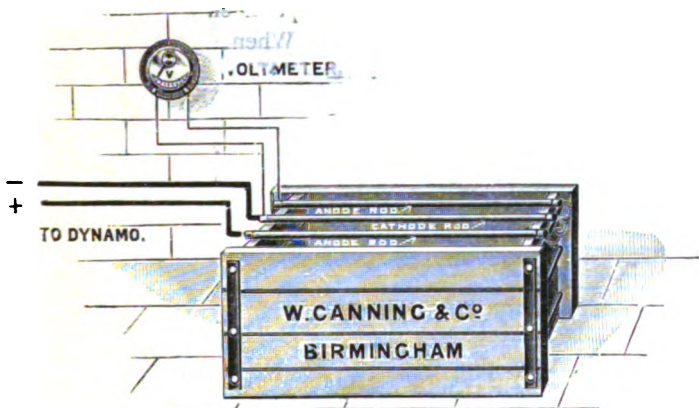


FIG. 48.—Voltmeter as a shunt across the bath.

which is being maintained at the bath terminals. Further reference to these instruments will be made in a subsequent chapter.

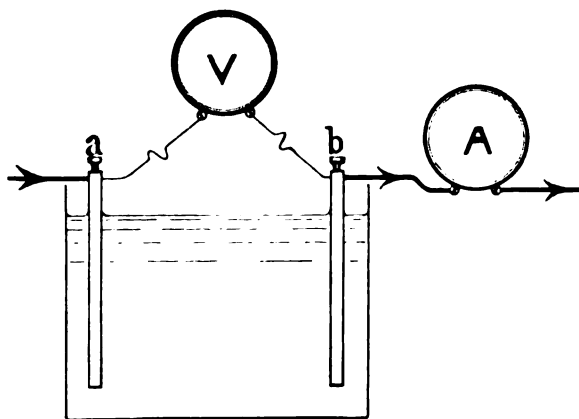


FIG. 49.—Showing connection of ammeter and voltmeter.

Generators in Parallel and Series.—Where cells or accumulators are being used, it becomes necessary to use a

number of them suitably arranged to yield the E.M.F. necessary to maintain deposition. The following table (III.) shows (only very roughly) the E.M.F.'s required for the different solutions under quite ordinary conditions, while in Table I. (p. 10) are shown the E.M.F.'s of the most common voltaic cells, of which the Bunsen, Smee, and the Daniell cells are more frequently used than others.

TABLE III.

E.M.F.s REQUIRED FOR ORDINARY PLATING SOLUTIONS.

Solution.	E.M.F.
Copper (acid bath)	0.5
„ (cyanide)	2-3
Brassing	3-5
Silver	1-2
Gold	1.0
Nickel	2-3
Iron	2-3

Now, the E.M.F.'s for the different solutions are really very elastic figures, depending upon the strength of solution, presence of free acid or cyanide, current density required, temperature, distance between anodes and cathodes, whether solution is at rest or in motion, and also on the solubility of the anodes. For the sake of example, however, the above figures will be quoted, though in a good cyanide copper solution, at about 50° C. and in motion, it is quite possible to maintain a current density (amperes per square foot) of 10 to 20 with a P.D. not exceeding 1 volt.

The point to observe is this: If, for ordinary working a nickel solution requires from 2-3 volts, an available E.M.F. of more than 3 volts is required. This E.M.F. would be forthcoming from two Bunsen cells or two accumulators, if these are connected in series.

Fig. 50 shows three cells or accumulators arranged in series.

The E.M.F. of the combination is three times that of one cell, or, in general, if E is the E.M.F. of one cell, then n cells in series have an E.M.F. of nE . Thus cells are arranged in series in order to produce higher E.M.F.'s. At the same time, however, if r is the resistance of one cell, then nr is the resistance of the combination, and thus on short circuit (that is, without external resistance) they produce—

$$C = \frac{\text{total E.M.F.}}{\text{total resistance}} = \frac{nE}{nr} = \frac{E}{r}$$

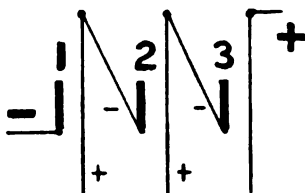


FIG. 50.—Three cells in series.

or the same current only as one cell if short-circuited. What then, it may be asked, is the value of the series combination? The answer is found when we remember that the combination of cells is not short-circuited, but is used on a circuit containing appreciable resistance. Call this R . Then for one cell only—

$$C = \frac{E}{r + R}$$

while for n cells—

$$C = \frac{nE}{nr + R}$$

Here the numerator has increased n times, but only a smaller part of the denominator has increased to the same extent. Test this by taking $E = 2$ volts, $r = 0.1$ ohm, and $R = 1$ ohm. Then for—

$$1 \text{ cell, } C = \frac{E}{r + R} = \frac{2}{0.1 + 1.0} = \frac{2}{1.1} = 1.82 \text{ amperes.}$$

$$2 \text{ cells, } C = \frac{2E}{2r + R} = \frac{4}{0.2 + 1} = \frac{4}{1.2} = 3.34 \text{ amperes.}$$

$$6 \text{ cells, } C = \frac{6E}{6r + R} = \frac{12}{0.6 + 1} = \frac{12}{1.6} = 7.5 \text{ amperes.}$$

Hence, to obtain the higher E.M.F.'s required for some

solutions, cells must be connected in series *until* that E.M.F. is obtained, but not beyond; for if three cells in series produce 6 volts when only 4 volts are required, the 2 volts must be wasted in the resistance. The third cell could be used to greater advantage in a manner which will shortly be indicated.

Again, for an ordinary copper sulphate bath a good current density can be obtained with, say, 2 volts, and in a

well-arranged vat as low as 0.5 volts should serve for a current density of 10 amperes per square foot. Assume that 2 volts are required. How should three accumulators be arranged in order to be most effective? The cells would best be connected in parallel. This arrangement is shown in Fig. 51,

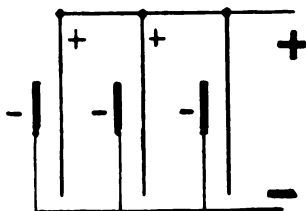


FIG. 51.—Three cells in parallel.

where all the positives are joined together to form a single positive pole, and all the negatives are similarly connected to form a common negative pole. This is the parallel method, and by it the E.M.F. of the combination is the same as that of a single cell, while the resistance of the combined cells decreases as the number of cells in parallel increases. Thus with n cells in parallel the resistance is $\frac{1}{n}$ th of that of one cell.

Similar calculations with the same values as those given above for cells in series then give—

$$1 \text{ cell } C = \frac{E}{r + R} = \frac{2}{0.1 + 1} = \frac{2}{1.1} = 1.82 \text{ amperes}$$

$$2 \text{ cells } C = \frac{E}{\frac{r}{2} + R} = \frac{2}{0.05 + 1} = \frac{2}{1.05} = 1.91 \text{ amperes}$$

$$6 \text{ cells } C = \frac{E}{\frac{r}{6} + R} = \frac{2}{0.016 + 1} = \frac{2}{1.016} = 1.97 \text{ amperes}$$

Now this arrangement does not seem to give a sufficient

increase in current. This is due to the very *high* resistance taken for the external circuit. Consider the external circuit now of low resistance, say, 0.05 ohm ; then with

$$1 \text{ cell } C = \frac{E}{r + R} = \frac{2}{0.1 + 0.05} = \frac{2}{0.15} = 13.3 \text{ amperes}$$

$$2 \text{ cells } C = \frac{E}{\frac{r}{2} + R} = \frac{2}{0.05 + 0.05} = \frac{2}{0.1} = 20 \text{ amperes}$$

$$6 \text{ cells } C = \frac{E}{\frac{r}{6} + R} = \frac{2}{0.016 + 0.05} = \frac{2}{0.066} = 30 \text{ amperes}$$

Much, therefore, depends upon the external¹ resistance, which *always* should be kept low, and it would be difficult to make a hard-and-fast rule for all cases unless the external resistance is specified. When this is known, the following general rule is applicable: that the greatest current is obtained when the internal and external resistances are equal, and if there is any deviation from this rule the error of adding too many in series should be made rather than that of too many in parallel.

Such is the usual rule for obtaining the maximum current from a set of cells. For plating purposes, however, a better rule to follow is that of arranging a sufficient number in series to produce the necessary E.M.F. and adding on the remainder judiciously in parallel. This involves connecting cells both in parallel and series. Fig. 52

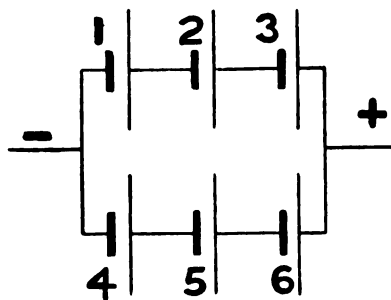


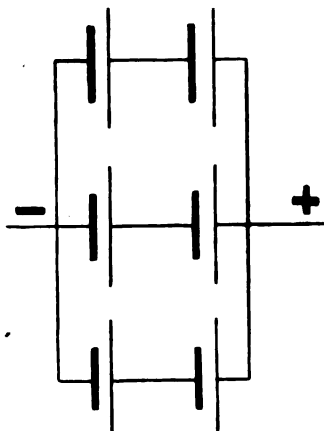
FIG. 52.—Cells in series and parallel.

shows such an arrangement. Here cells 1, 2, and 3 are

¹ External resistance here means resistance external to the cell. This should mainly consist of the resistance of the bath.

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arranged in series; cells 4, 5, and 6 form another group of three in series. These two groups are now paralleled as



shown. Regard each group as a single cell of E.M.F. = $3E$ volts and resistance of $3r$. Then by paralleling two such groups the E.M.F. is unaltered, viz. $3E$, while the resistance is halved, viz. $\frac{3r}{2}$, and hence the total current with external resistance R would be—

$$C = \frac{3E}{\frac{3r}{2} + R}$$

FIG. 53.—Cells in series and parallel.

In this arrangement there are said to be *three* in series

and *two* in parallel, the two referring to sets of three in series, and not to single cells.

Similarly Fig. 53 shows the arrangement of the same number of cells in a different manner. In this case there are two in series and three (sets of two in series) in parallel. The

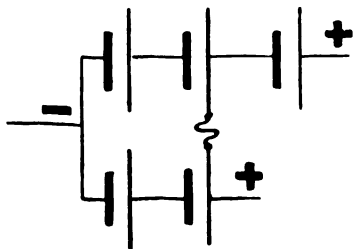


FIG. 54.—Cells in series and parallel.

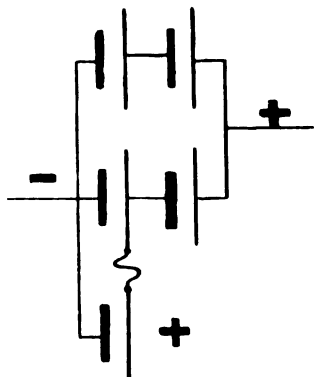


FIG. 55.—Cells in series and parallel.

E.M.F. of the combination is $2E$ volts, and the resistance is $2r$.

3. An important point in paralleling cells must not be overlooked. *Only cells of the same E.M.F. must be put in parallel.* Three in series must not be put in parallel with two in series. In the case of an odd number of cells the further arrangements (Figs. 54 and 55) may be regarded as typical of the possibilities.

Arrangement of Accumulators for Varying E.M.F.'s.

In many workshops, however, the dynamo serves as the source of current, and is usually supplying a number of vats requiring different E.M.F.'s. For this purpose its E.M.F. should be a little in excess of the highest required, and for those vats requiring a lower E.M.F., reduction must be effected by resistances. Where, however, accumulators are in use, more economy can be exercised in the distribution of E.M.F. Suppose we have to deal with four accumulators giving normally 8 volts.

For brassing, these must be connected in series. For copper sulphate work the E.M.F. (8 volts) would be much too high. Rearrangement in parallel

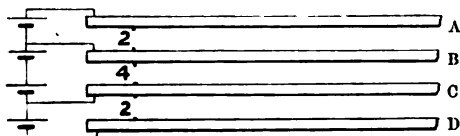


FIG. 56.—Arrangement of accumulators and conductors for different voltages.

could not be readily effected, and if it were done by a mercury switchboard it would make the combination useless for brassing. The difficulty can be surmounted in the following way as shown in Fig. 56.

The cells are connected in series. Then four copper bars may serve as conductors of current to the various parts of the workshop or laboratory. These are connected as follows: Bar A is joined to the + of 1, and B to the - of 1 (or + of 2).

Between A and B there is one accumulator (= 2 volts). D is joined to the - of 4 and C to the + of 4 (or - of 3). Between C and D there is one cell (= 2 volts). Similarly between B and C there are two accumulators, equal to 4 volts. Hence, using the following pairs of bars, we have—

A and B	2 volts with A +
B „ C	4 „ „ B +
C „ D	2 „ „ C +
A „ C	6 „ „ A +
A „ D	8 „ „ A +
B „ D	6 „ „ B +

This choice of voltage, viz. 2, 4, 6, or 8, considerably diminishes the necessity for resistances, and economizes the capacity of the accumulators.

A similar arrangement for six accumulators is shown in Fig. 57. Here—

A and B	give 2 volts with A +
B „ C „	6 „ „ B +
C „ D „	4 „ „ C +
A „ C „	8 „ „ A +
B „ D „	10 „ „ B +
A „ D „	12 „ „ A +

And thus with an easy change of connections the choice of 2, 4, 6, 8, 10, or 12 volts is obtained, and the saving effected is such that if only 2 volts are required in one vat they are obtainable from one cell, and the current used passes through and impoverishes only that cell. Without such an arrangement, whatever current is used passes through *all* the cells and reduces their content of available energy, while at the same time the unnecessarily high E.M.F. has to be cut down and electrical energy thus lost by a large external resistance. Where cells are used separately, strict care must be exercised that they are not reduced below 1·85 volts. A convenient check can be held on them by means of a voltmeter

with a suitable switch. Fig. 65 (p. 83) shows a sketch of such a switch, and by it the E.M.F. of any cell can be read, and when this falls to 1.85 the cell must be no longer used. Discretion must be shown to so use the cells that they may all be ready for recharging at about the same time.

The easy change of voltage may be made simply by altering the main conductors of the vat into the different connecting screws soldered or screwed on to the conducting bars as shown

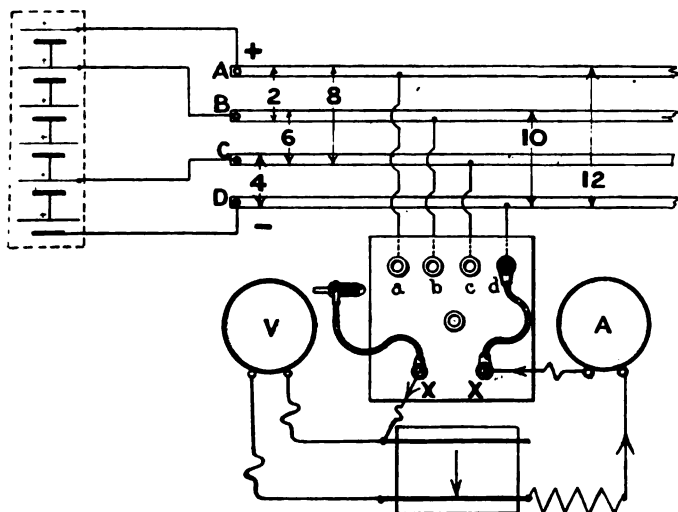


FIG. 57.—Arrangement of six accumulators to four conducting bars to give 2, 4, 6, 8, 10 or 12 volts, with plug board, and connections to a simple plating circuit.

in Fig. 57. A convenient method is that of using a plug board, also shown in Fig. 57. This may be of slate, and containing five tapering brass plug holes. Four of these are permanently connected to the bars A, B, C, and D. The fifth has no connection. The vat leads are attached to the terminal screws X, X, from which two flexible leads terminating in tapering plugs are connected. These plugs may now be placed in the tapering holes, using the pair which will give the required

E.M.F. In addition to the different voltages, the direction of the current may be reversed if necessary, and to cut off the current one of the plugs may be placed in the fifth and unconnected hole. The sizes of the plugs, holes, and leads must be controlled by the current to be carried.

Arrangement of Vats.—In a workshop, five or more different solutions may be in use, viz. copper, acid and cyanide, brassing, gilding, silver, nickel, iron, and perhaps tin and bronze. It is, of course, well known that these must not be placed in series, for then—

- (1) The current would be the same in each vat.
- (2) If one vat is out of use, it must be short-circuited or the current is at once stopped in all the vats.
- (3) A defective connection in one vat would similarly influence the current in all the others; and
- (4) The E.M.F. of the generator would need to be the sum of the E.M.F.'s required for the separate solutions.

Arranging in parallel has the following advantages:—

- (1) The E.M.F. of the dynamo need be equal only to the highest required for any solution.

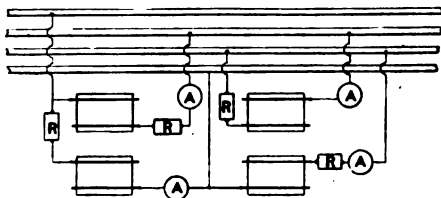


FIG. 58.—Arrangement of four vat circuits to conducting bars for different voltages.

- (2) Each vat can be used quite independently of the others.

- (3) Vastly different currents may be used in each, the control in any one vat barely influencing the others.

For this system, however, there should be for convenience and for intelligent working, a separate resistance and ammeter for each vat. Such an arrangement for four vats is shown in Fig. 58. If, as in this diagram, the four bars conduct the current from a system of accumulators, the choice of E.M.F.

available permits of the more economic use of the current by a diminished waste in resistances. Further, while the main leads are heavy, those for the separate vats will be selected according to the current to be used in the vats, and in these days of cheap and reliable instruments no vat should be without its ammeter, and, though less important, its resistance. We are long past the day when the current passing through a vat is estimated by the spark it will produce by short-circuiting.

Voltmeter.—Up to the present little has been said about the use of this instrument. Its importance cannot be over-estimated. Connected as a shunt across the vat terminals it records their difference of potential, or, in other words, the E.M.F. which is being used to drive the electricity through the solution. Hence according to Ohm's law, viz.—

$$E \text{ (volts)} = C \text{ (amps.)} \times R \text{ (ohms)}$$

$$\text{or } C \text{ (amps.)} = \frac{E \text{ (volts)}}{R \text{ (ohms)}}$$

its reading taken in conjunction with that of the ammeter indicates the resistance of the bath. Thus if in two baths in series the readings on voltmeters are 2.2 and 4.4, then in the latter there is twice as much resistance as in the former. The resistance of a solution is influenced by many circumstances, among them being (1) strength of solution, (2) amount of free cyanide or acid, (3) distance apart of the electrodes, (4) temperature, and (5) the effective solution of the anodes or otherwise. Hence to maintain a constant current density will demand a different P.D. under these differing conditions, and regarding a constant current density as desirable and even ideal, an attempt to maintain it by a constant current as recorded on the ammeter will at once reveal any defect in the previously mentioned conditions by the reading on the voltmeter. Suppose that in a silver solution, it is found that when a desirable current density is being used a P.D. of 1.5 volts is recorded on the voltmeter. On some subsequent occasion, when the same C.D. is being employed, a higher

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reading, say, 2.0 or 2.5 volts, may be found on the voltmeter. This at once shows an increased resistance in the vat most probably due to poor connections or a lack of free cyanide. In the latter case, the addition of more cyanide, especially around the anode, will at once reduce the P.D. required to maintain the constant current density, and the solution is thus corrected. So useful in fact is the voltmeter that it may be used to great advantage even without an ammeter. To illustrate this assume the following conditions: (1) A cathode surface producing a resistance of 1 ohm, (2) 10 amperes as the desirable current for this surface. Hence P.D. = 10 volts. Sum the remainder of the resistance as external resistance. At first, let this also be 1 ohm. We have then the following:—

VAT.			EXTERNAL.		
R.	P.D.	C.	R.	P.D.	C.
1	10	10	1	10	10

By doubling the cathode surface we practically halve the resistance of the vat,¹ and the current is thereby increased in the whole circuit, for now

$$\begin{aligned}\text{Total current} &= \frac{\text{total E.M.F.}}{\text{total resistance}} = \frac{20 \text{ volts}}{1 + 0.5} \\ &= \frac{20}{1.5} = 13.3 \text{ amperes}\end{aligned}$$

The total E.M.F. is now distributed proportionately to the resistance, and for each part of the circuit can be calculated by $E = C.R.$ thus—

$$\begin{array}{ll}\text{Vat} & E = 13.3 \times 0.5 = 6.66 \\ \text{External} & E = 13.3 \times 1 = 13.3\end{array}$$

¹ This is not strictly true, but is near enough for our purpose now.

Hence, keeping the figures in the same order, we have—

0.5	6.66	13.3	1	13.3	13.3
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The increase in ammeter reading and decrease in voltmeter reading are readily observable.

For the increased surface, however, 13.3 amperes does not maintain the current density. To do this the current should be increased to 20 amperes, and this by reducing the external resistance to 0.5 ohm; then—

0.5	10	20	0.5	10	20
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In thus reproducing the correct C.D., the P.D. at vat terminals is brought back to the original, and this shows that under the best conditions a constant C.D. is maintained by a constant P.D. It must be observed, however, that this applies only to the case where the main resistance in the bath is that of the solution. If the contacts are poor, then the resistance is not reduced proportionately with the increased cathode surface. These contact resistances will thus be much more marked when the work is increased in the bath, and hence more than the anticipated E.M.F. will be required, and as these contact resistances are ever present, however small, the above rule of a constant P.D. for constant C.D. does not quite hold good, and for larger areas of cathode surface a slightly higher P.D. is needed.

The principle allows of the use of a voltmeter without an ammeter, involving only a simple reading by which the correct conditions are indicated. The method has therefore much to recommend it, especially in view of the fact that a single voltmeter may be used for a number of vats by means of a switch similar to that shown on p. 83.

The following table (IV.) illustrates the conditions in two different baths :—

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TABLE IV.

SHOWING DIFFERENT P.D.'s AT TERMINALS OF VATS IN GOOD AND BAD CONDITION FOR THE SAME CURRENT DENSITY.

I. [CLEAN].				II. [DIRTY].			
Area of cathode. sq. ins.	C.D. required.	C. passed.	P.D.	Area of cathode. sq. ins.	C.D. required.	C. passed.	P.D.
(1) 5.25 10.5	10 10	0.36 0.73	0.26 0.29	5.25 10.5	10 10	0.36 0.73	0.47 0.53
(2) 5.25 10.5	20 20	0.73 1.46	0.43 0.45	5.25 10.5	20 20	0.73 1.46	0.90 1.15
(3) 5.25 10.5	30 30	1.09 2.18	0.70 0.72	5.25 10.5	30 30	1.09 2.18	1.20 1.55

Vat I. had all soldered connections and clean anodes, while in Vat II. the connections were made less perfectly and the anodes were not particularly clean. The figures well illustrate the point.

In the following chapter attention will be directed more especially to the matter of the collection of the current from the generator, and its distribution to the various parts of the workshop.

CHAPTER V

Switchboard and Connections

Introduction.—In a workshop of any considerable size in which different classes of work are done, and where current may be required at all times, arrangements of a somewhat more special character than those outlined in Chapter IV. are necessary. Thus if power is only available during the daytime, and current is required for deposition during the night, accumulators must be used in addition to the dynamo. In such works a considerable amount of time may be saved by allowing thick deposits to be slowly produced during the night. The vats are thus able to turn out more work than if standing idle during that time, or, to put it in another way, the size of the plant to turn out a given amount of work will be kept down, involving less capital outlay. This can easily be accomplished by charging accumulators during the daytime while power is available, and using them for the night deposition. Further, where the deposition of different metals is being carried on at the same time, the different voltages which they require can be put on to their mains from such accumulators, involving a greater economy of current and better control over the different branches of the circuit. Such an arrangement will involve more complex connections with frequent changes of leads. In order to do this quickly and effectively, to gather up the current from the different generators—the dynamo and accumulators—to distribute it to the several branches of the divided circuit, to measure and to control it, the connections should be conveniently arranged, so

that they may be quickly made and changed. They are usually brought together on a wood, slate or marble board, called the **switchboard**. The whole of the current and the parts in the several branches of the circuit are thus readily observed and controlled. The number of contacts to be made and broken are reduced to a minimum, and those made permanently can be well protected from the corrosive fumes which are always present in or near the plating-room.

The Switchboard is therefore the slab of wood, slate, or marble on which the various switches, instruments, and even resistances can be suitably mounted. It must, obviously, be made of some non-conducting medium, and should possess the following properties :—

(1) **High insulation**, to prevent leakage. This cannot be obtained with wood, though wood, well paraffined, might be used for boards on which currents of low voltage, say, for plating purposes, are being dealt with. Even then, wood is so apt to absorb moisture and liquids, which are ever present in plating workshops, that even on low voltages leakage soon occurs. A more suitable material is therefore slate or marble. Slate may be either dull or enamelled, and marble dull or polished. These substances have high insulation properties, and do not absorb the moisture which collects upon them. They are both easily worked, drilled, etc., for connections, and may be mounted either with or without wood (usually teak) or metal frames.

(2) **Non-inflammable**.—This is especially desirable where heavy currents are being used for a long time. Conductors becoming warm unavoidably, might readily ignite the combustible gases expelled from heated wood, and resistances would need to be mounted some distance away. These troubles do not arise where non-inflammable materials are used. Such materials may be then mounted in frames of wood or iron—preferably the latter.

In erecting switchboards a good allowance of room should be made behind them, in order to facilitate access to the

connections on the back. Where a large board is required, it may be suitably divided, for convenience, into panels. All connections upon it should be arranged with a minimum of crossing, and crowding of the connections must be avoided. The connections for different parts of the circuit may be arranged on different panels, always having in mind some idea of symmetry.

Switches should be arranged in each branch of the circuit. By them the current can be completely cut off from that part of the circuit. By means of a switch, the dynamo may be put on to the accumulators for charging, or may be connected to the conductors passing to the workshop. By them, also, the accumulators may be entirely cut off from every part of the circuit when not in use. This prevents running down by leakage through vats, or through connections accidentally made and overlooked. Switches are usually of brass, on account of the ease of working that metal, though the heavy plain bar or "brush" is made of best electrolytic copper. This brush slides into elastic contacts, and is controlled by an insulating handle. Fig. 59 shows a single pole switch. A double pole switch has the advantage of entirely cutting off the several parts of the apparatus. Single pole switches cut off only one side, and while the circuit is broken the connection on the other side still remains for any leakage which may result from some source of higher E.M.F. in the vicinity.

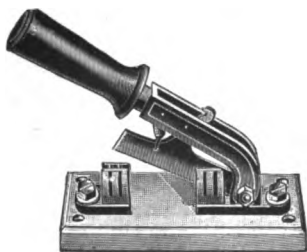


FIG. 59.—Single pole switch.

Instruments are required on the switchboard for the following purposes :—

(1) **Ammeters**—

- (a) To give total output of dynamo.
- (b) To record charging or discharging current of the accumulators.

- (c) To show the current in the shunt circuit of the machine.
- (d) To record the current passing into the several main sets of conductors.
- (2) **Voltmeters**—
 - (a) To indicate the total volts of the machine.
 - (b) To record by a suitable switch the E.M.F. of any of the accumulators separately, so that defects in them will at once become obvious.

Resistances can be mounted a short distance from the board, and the various points brought to studs mounted on the switchboard, over which the regulating arm moves. Such connections must, of course, be made of suitable dimensions, having in view the current to be carried. Our purpose now is to indicate arrangements rather than details of erection. Small resistances, such as might be used in the shunt circuit of the dynamo, can be at once mounted on the back of the board, the regulating arm passing over studs arranged in a semicircle or arc on the front.

Diagrams of Switchboards and Connections.

The following diagrams are intended to show the connections of boards for workshops of different requirements. If these few examples are understood, little or no difficulty will be experienced in extending the ideas.

Fig. 60 shows the dynamo, D, arranged for connection to the workshop circuit by means of the double pole switch, DP.¹ The ammeter, A, records the total current, and the voltmeter, V, shows the P.D. at the dynamo brushes. The whole of these connections are permanently made behind the board.

In Fig. 61 the two separate branches are provided with switches and ammeters. Each branch may therefore be used

¹ The DP switches are conveniently shown with only four points, the two on which the switch is pivoted being omitted.

independently of the other, and the current in each branch separately recorded. The voltmeter, V, records the P.D. at dynamo terminals, and the vats are arranged with their individual resistances and ammeters on to the leads, L, L.

To allow for shunt regulation, a small resistance placed on

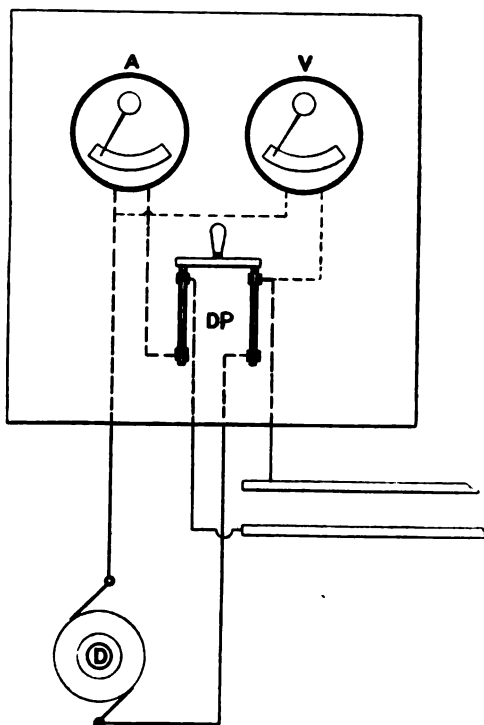


FIG. 60.—Switchboard for single circuit.

the board is convenient. This is shown in Fig. 62. D represents the commutator and brushes of the dynamo, from which the main conductors and double pole switch with ammeter A will be seen. The shunt-winding of the dynamo is shown diagrammatically at S, and in this circuit is placed the ammeter As, which records the current in the winding, and the resistance

R, which regulates it. Only the studs and arm of the resistance are shown. The small coils of German silver wire behind the slate would appear as in Fig. 62 (inset). This shunt resistance regulates the current in the winding of the field magnet, and therefore the strength of the magnetic field

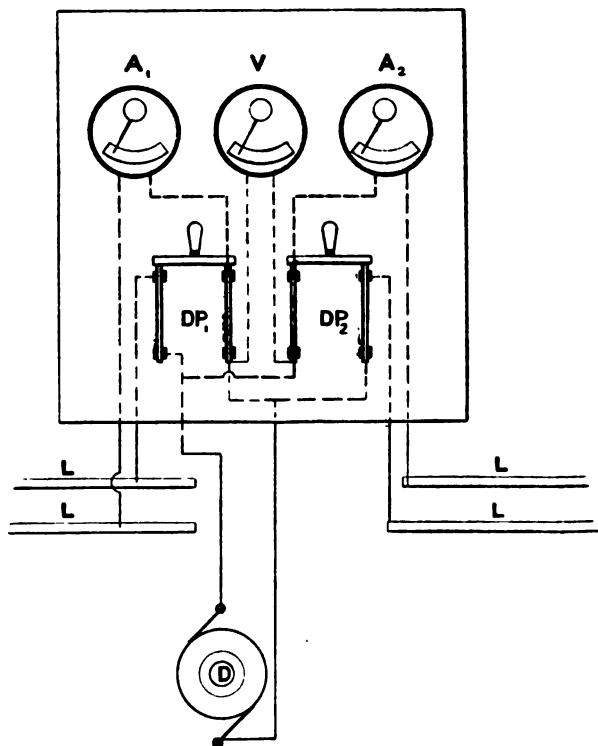


FIG. 61.—Switchboard for two separate circuits.

and the rate at which lines of force are being cut, and hence the E.M.F. of the machine, and, finally, the current in the whole of the circuit. With large-current machines a little regulation here saves very much bigger resistances in the main circuit.

Dealing now with the case where accumulators are added

to the installation, it will be seen at once that the following connections must be easily made :—

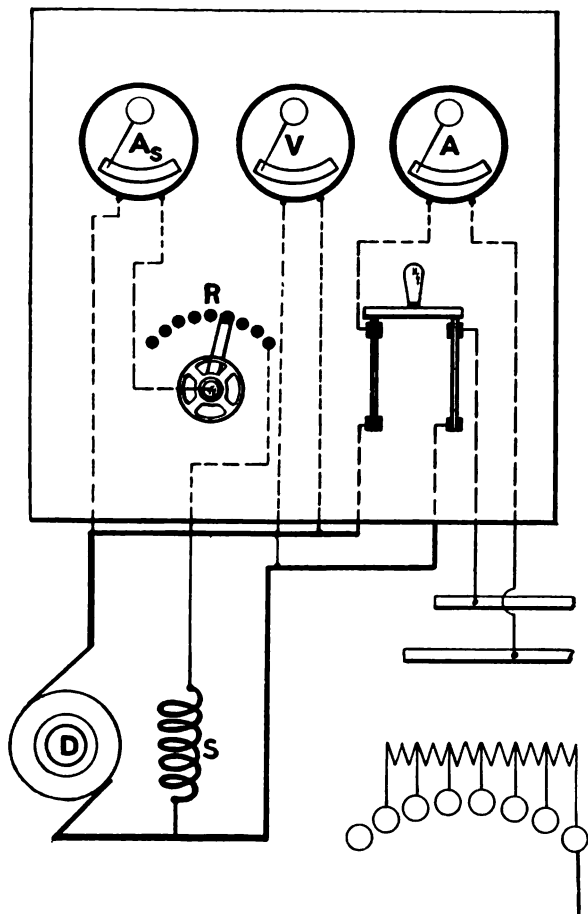


FIG. 62.—Switchboard with connections for regulation of current in shunt winding.

(a) For the dynamo to supply current to the workshop circuit and accumulators either separately or simultaneously.

(b) For the workshop conductors to receive current from the machine or the accumulators. Where accumulators are being charged, a resistance in the circuit will enable the charging current to be controlled without having to alter the P.D. of the machine, and therefore the current in the workshop circuit. Further, connections might be made to admit of charging the accumulators altogether or in sections. Most usually it

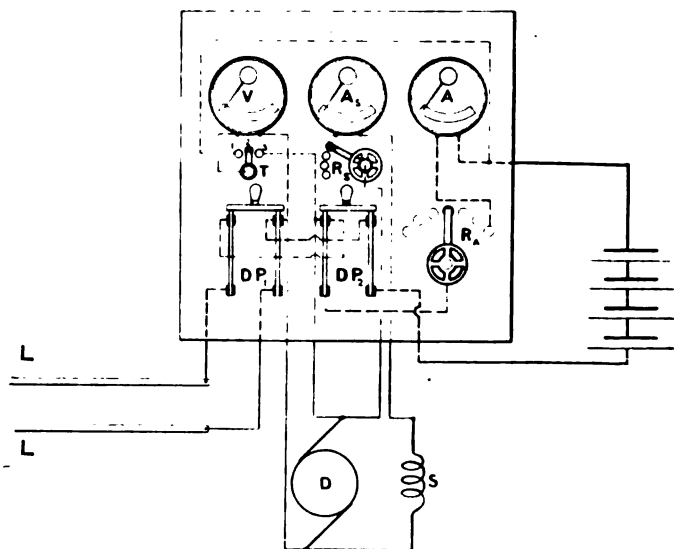


FIG. 63.—Switchboard with connections for charging and using current from four accumulators.

would be convenient to charge them in series and make allowance for drawing off the current from them singly or in sets of two or three in series. The arrangement in Fig. 63 only allows of their being charged and discharged together. In this diagram—

D = commutator of machine.

S = shunt winding with resistance R_s and ammeter A_s .

DP_1 is a double-pole switch which allows the connection

of the machine with the workshop circuit on to the leads, L, L.

DP_2 is another double-pole switch which puts the machine on to the accumulators, the current flowing through the resistance R_a of suitable design and carrying capacity, and through the ammeter A. A and R_a thus measure and control the current which passes through the accumulators.

When both DP_1 and DP_2 are in, the machine supplies current for charging accumulators and also to the workshop leads, and either switch can be used separately for its own purpose. To use the current from the accumulators on to the workshop leads would involve first taking off one set of brushes from the commutator and cutting out the shunt winding at Rs . Current would then flow from the cells through DP_2 and DP_1 to the leads and be measured by A and controlled at R_a . One other useful connection is the 2-way switch at T. When the arm is on stop 1 the P.D. across the four cells is measured. When on stop 3 the P.D. of the machine is shown; while 2 is an off stop. It need hardly be added that for this purpose the machine should have a voltage of a little more than 4×2.5 volts, 2.5 volts being the maximum required for completely charging each cell. Further advantages might now be aimed at by increasing the range of volts available on the workshop leads and by a special switch for indicating the P.D. of each cell separately. This is shown in Fig. 64.

In this figure the shunt winding, ammeter, and resistance have been omitted in order to reduce the connections to a minimum. The dynamo leads are joined to DP_1 and DP_2 . From DP_1 the cells are charged using the resistance R_a and ammeter A_1 .

From DP_2 conductors convey the current to the two outer conducting leads so that the dynamo can be put on to them, and the current read at A_2 . It is only when the accumulators are in use that variation of E.M.F. can be obtained. If now the dynamo brushes are raised, then by putting DP_1 and DP_2 in, the current from the four cells in series is put on to the

outer workshop bars, yielding 8 volts. If now an additional lead be taken from the - of cell 3, or + of cell 2, through a S.P. switch on the board to the middle workshop bar, then we shall have—

Bars X and Y	4 volts with X positive
„ Y and Z	4 „ „ Y „
„ X and Z	8 „ „ X „

The ammeter A_2 will now only serve to measure the current

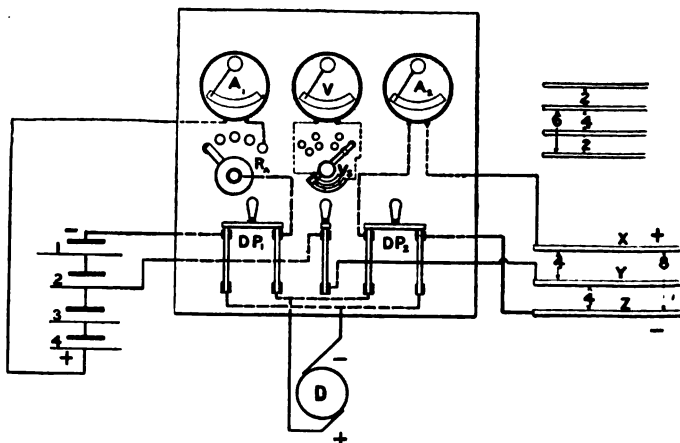


FIG. 64.—Switchboard with connections for charging accumulators and utilizing them for varying voltages.

passing through circuits on to the bars XY or XZ. It does not measure current passing between the conductors YZ. It will also be seen that by introducing two bars between X and Z we might arrange for the following voltages, as shown in inset. Further, by increasing the number of cells, greater variation can be obtained, as shown in Chapter IV. In any case, where cells are used separately, every attempt should be made to use them as uniformly as possible so that they may require the same amount of charging. In order to keep a watchful eye on the accumulators, a simple switch can be made

after the pattern shown at Vs, the details of which are set out in Figs. 65 and 66. There are four pairs of studs arranged as shown and connected to the cells by thin wires as indicated. M and N represent two curved bars fixed to the slate base and connected behind to the voltmeter. The moving arm of the switch is a double one, the two parts being separated by insulating material. When the switch is in the position shown on the diagram, the terminals of accumulator No. 1

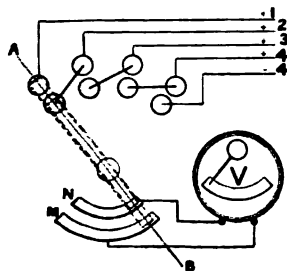


FIG. 65.—Voltmeter switch.



FIG. 66.—Voltmeter switch.

are directly connected to the voltmeter, and the P.D. of the cell is read. By moving the switch on to the other pairs of studs the P.D. of the cells can be read separately, whether the cells are idle or sending current. Such a simple plan enables the condition of the cells to be carefully watched, and steps may at once be taken to correct any error which may be discovered.

Sufficient has now been given to show the manner in which the usual workshop connections can be systematically and conveniently made. Should it be thought, however, that such arrangements are costly and thus beyond the reach of ordinary works, it may still be urged that similar schemes of connections can be followed out in perhaps not quite so compact a form, by means of simple switches of the home-made type. There is room for much advance in this direction in many of our workshops.

CHAPTER VI

Resistances

WHERE electro-deposition is being carried out on a small scale, with a fairly constant E.M.F., such as would be derived from a system of accumulators or a dynamo, and varying cathode area, a constant current density is not easy to maintain. Yet it is essential for maintaining uniform deposition, especially where slight changes of current density considerably affect the character of the deposit. Under these circumstances some easy means of regulating or controlling the current is desirable. Resistances are used for this purpose. Where deposition is being carried out on a larger scale, slight variations in the cathode area do not appreciably affect the current density, and hence external regulation of the current is not so necessary. Now, the current can be controlled in several ways, thus—

(1) By varying the intensity of the magnetic circuit of the generator by regulating the current on the shunt coils.

(2) By adding resistance to the circuit usually in the form of coils of wire.

(3) By altering the resistance of the bath by varying the distances between anodes and cathodes.

The usual arrangement of a vat is such that, except on a very small scale, method No. 3 becomes impracticable. Method No. 1 might be much more frequently and advantageously used than it is. Method No. 2 is the one most commonly employed and to which attention is now directed.

Definitions. — By resistance we mean the opposition offered by substances to the passage of electricity. It varies

very considerably in different substances. Copper and silver are the best conductors, that is, they offer the least resistance, while dilute sulphuric acid (1-10) offers about 1,000,000 times as much resistance as silver, and pure water about 15,000,000,000,000 times as much. Substances which do not allow current to pass through them appreciably are called **insulators**.

The **Unit of Resistance** is termed the **Ohm**, and is the resistance offered by a column of mercury 106.3 cm. long and 1 sq. mm. in cross-section at a temperature of 0° C. In a more understandable and practical form we may say that it is the resistance through which an E.M.F. of 1 volt is spent in maintaining a current of 1 ampere.

The relative powers of the metals for allowing the electric current to pass are shown in Table V.

TABLE V.

RELATIVE CONDUCTANCE OF METALS.

Silver	100	Iron	16.7
Copper	100	Nickel	13
Gold	78	Lead	7.5
Aluminium	55	Antimony	4.3
Zinc	28	Mercury	1.6
Platinum	19.5	Bismuth	1.2

Their relative resistances are in the reverse order. For ordinary conductors we combine good conducting powers with cheapness, and hence the extensive use of copper, closely followed by aluminium, for while aluminium is so far behind copper in its conducting power, it must be remembered that the above figures refer to the same length and area of the conductors, and as aluminium is only one-third of the weight of copper, and its cost about the same, aluminium has quite as good conducting power, if not better, when we compare equal weights of the metals or equal monetary values.

When, on the other hand, we require a substance to add resistance to the circuit, we select a metal of poor conducting power. Of the metals quoted above, platinum is too expensive

except in rare instances. Nickel is much more costly than iron, lead is not sufficiently strong for practical purposes. Antimony and bismuth do not ordinarily occur in the convenient form of wire, and mercury is quite out of the question. For ordinary resistances, therefore, iron wire is frequently used, though it offers the disadvantage of considerable corrosion, especially in contact with acid fumes. A number of alloys, however, have high resistances, and the following figures show their conducting powers to the same standard as those above.

German silver (Cu 60, Zn 25, Ni 15)	5.00
Platinoid (German silver with a trace of tungsten)	3.75
Manganin (Cu 85, Mn 12, Ni 3)	3.00

These metals are therefore largely used for small resistances, more especially for experimental purposes.

Variation of Resistance.—The resistance of a wire depends upon a number of circumstances.

(1) **Length.**—Resistance is proportional to length. The resistance of 100 yards is five times that of 20 yards of the same wire.

(2) **Sectional Area.**—Experiment shows that the thicker the wire, the less is the resistance, even though there is in the same length more metal. The resistance, however, is not diminished proportionately with the increased thickness, but with the square of the thickness or with the sectional area. Thus taking wires of *same material and length*, if the resistance and thickness are compared, we have the following results:—

Thickness (d).	Resistance (R).	
1	1	$\left. \begin{array}{l} \\ \\ \\ \\ \\ \end{array} \right\} \begin{array}{l} \text{so that} \\ R \times d^2 = \text{const.} \end{array}$
$\frac{1}{2}$	4	
$\frac{1}{3}$	9	
$\frac{1}{4}$	16	
$\frac{1}{5}$	25	
$\frac{1}{10}$	100	

The resistance is thus said to be inversely proportional to the square of the thickness, or to the sectional area.

Consider a circular wire of thickness d . The area of the section is $\frac{\pi d^2}{4}$ or πr^2 , and the less this quantity becomes, so proportionately greater does the resistance become.

Combining these two principles we say that

$$\text{Resistance} \propto {}^1 \frac{\text{length}}{\text{area}} \text{ or } \frac{l}{\pi r^2}$$

(3) **Material:** for there is a great difference between platinum and copper. In order to compare the metals quantitatively we must make the necessary allowance for other conditions, and for this purpose it is usual to compare the resistances of small cubes of the metals of 1 cm. side, that is, 1 cm.³

The resistance of these small cubes is called the **specific resistance**, and as in all cases it is small, it is more usual to express it in **microhms** (1 microhm = $\frac{1}{1,000,000}$ ohm). The specific resistances of the metals are seen in Table VI.

TABLE VI.

SPECIFIC RESISTANCES OF METALS.

Silver	1·6	Lead	20
Copper	1·6	Antimony	35
Gold	2·06	Mercury	100
Aluminium	2·9	Bismuth	130
Zinc	5·75	German silver	32
Platinum	8·2	Platinoid	42·5
Iron	9·6	Manganin	53·3
Nickel	12·4		

From these figures we may now calculate the resistance of any of these wires of known length and thickness. Thus—

¹ Means “proportional to.”

$$\left. \begin{array}{l} \text{Total resistance} \\ \text{(microhms)} \end{array} \right\} = \text{specific resistance} \times \frac{\text{length (cms.)}}{\text{area (cm.}^2\text{)}}$$

$$R \text{ (ohms)} = K \times \frac{l}{a} \times \frac{1}{1,000,000}$$

where

K = specific resistance (microhms)

l = length in cms.

a = sectional area in sq. cms. (cm.²)

and

1,000,000 = microhms in one ohm.

Example.—Calculate resistance of a copper wire 10 metres long and 1 mm. in diameter.

Now $K = 1.6$ microhms

$l = 10 \times 100$ cms.

$$a = \pi r^2 = \frac{22}{7} \times \left(\frac{1}{2} \times \frac{1}{10} \right)^2 = \frac{22}{7 \times 400}$$

$$\begin{aligned} \text{Hence } R &= \frac{1.6 \times 10 \times 100 \times 7 \times 400}{22 \times 1,000,000} \\ &= 0.2036 \text{ ohm.} \end{aligned}$$

Example.—What is the resistance per mile of 16 S.W.G. copper wire?

Now 16 S.W.G. wire = 0.162 cm. thick

Hence $K = 1.6$ microhms

$l = 1 \times 1760 \times 3 \times 12 \times 2.54$ cms.

$$a = \pi r^2 = \frac{22}{7} \times \left(\frac{0.162}{2} \right)^2$$

$$\begin{aligned} \text{Hence } R &= \frac{1.6 \times 1760 \times 3 \times 12 \times 2.54 \times 7}{1,000,000 \times 22 \times 0.081 \times 0.081} \\ &= 12.5 \text{ ohms.} \end{aligned}$$

Example. — How many yards of German silver wire ($K = 32$) of 18 S.W.G. will be required for a resistance of 20 ohms?

Now 18 S.W.G. = 0.122 cm. thick.

Hence
$$a = \pi r^2 = \frac{22}{7} \times \left(\frac{0.122}{2} \right)^2$$

$$R = \frac{K \times l}{a \times 1,000,000}$$

from which
$$l = \frac{R \times a \times 1,000,000}{K}$$

$$\therefore l \text{ (cms.)} = 20 \times \frac{22}{7} \times \frac{0.122 \times 0.122 \times 1,000,000}{2 \times 2 \times 32}$$

Dividing by $2.54 \times 12 \times 3$, l will then be given in yards.

$$\begin{aligned} \text{Hence } l \text{ (yards)} &= 20 \times \frac{22}{7} \times \frac{0.061 \times 0.061 \times 1,000,000}{32 \times 2.54 \times 12 \times 3} \\ &= 80 \text{ yards.} \end{aligned}$$

Many other examples might be given, but a few will suffice to show the method of working.

(4) Effect of Temperature.—Still another condition influences resistance, viz. temperature. As a rule the resistance of a solid is increased with a rise in temperature. Carbon forms an exception to the rule, as it behaves like a solution in having a smaller resistance at higher temperature. The increase of resistance of heated metals is not the same in every case. The following table shows the **fractional** increase of the resistance at 0°C. for every degree Centigrade rise in temperature. It now becomes obvious, that if temperature influences resistance, the specific resistances of the metals already given should be accompanied by a note of the temperature at which they are taken. The specific resistances given above are at 0°C. The fractional increase per degree C. for the metals is shown in Table VII.

TABLE VII.

TEMPERATURE COEFFICIENTS OF METALS AND ALLOYS.

Silver	0.004	Lead	0.00411
Copper	0.00428	Antimony	0.00389
Gold	0.00365	Mercury	0.00072
Aluminium	0.00423	German silver	0.00036
Zinc	0.00406	Platinoid	0.00031
Platinum	0.00247	Manganin	0.00000
Nickel	0.00620		

These numbers are termed "*temperature coefficients.*" It will be noticed that of the single metals mercury suffers the least change. The high resistance alloys have low coefficients, while manganin is unique in showing no change of resistance with temperature. Such an alloy is therefore invaluable for accurate resistances with which a rise of temperature will produce no change in the resistance.

Resistances in Series and Parallel.—When two resistances are put in **series**, the resistance of the combination is obviously the sum of the separate resistances. Thus two five-ohm coils in series are equal to one ten-ohm coil.

When placed in **parallel** a very different case presents itself. Thus, imagine two wires, *a* and *b*, of one ohm each, placed in parallel. Think of them from the point of view of their ability to convey electricity. Whatever opportunity there is for current to pass through the one is offered by the other, and hence through the two wires in parallel, current can flow with twice the facility as through one. In other words, the resistance of the combination is half an ohm. If *R* represents the resistance, then $\frac{1}{R}$ represents the conductance, that is, the ability to convey current. Two such wires, therefore, show a conductance of $\frac{1}{R} + \frac{1}{R} = \frac{2}{R}$, and inverting this we get the resistance = $\frac{R}{2}$, that is, one half of the resistance of a single wire. The same rule applies with a number of wires in parallel. Thus if three wires have resistances of 1, 2, and 3 ohms respectively, then when joined in parallel, their total resistance is found as follows:—

Let	$R = \text{total resistance}$
and	$\frac{1}{R} = \text{total conductance}$
Then	$\frac{1}{R} = \frac{1}{1} + \frac{1}{2} + \frac{1}{3}$ $= \frac{6 + 3 + 2}{6} = \frac{11}{6}$

Hence $R = \frac{6}{11}$ ohm, and, in general, any large resistance added in parallel to a smaller one gives a further decreased resistance in the combination.

Carrying Capacity of Wires.—Before applying the foregoing information a further matter must demand attention. While in a resistance we aim at getting the maximum resistance in the cheapest way, yet it must be remembered that possibly such a resistance may be required to carry heavy currents. High resistance could soon be obtained with thin wires, but their **carrying capacity** for current would be very small and the fine wires therefore unserviceable. The carrying capacity is measured in terms of the current which may be carried without producing an undue rise in temperature. This applies also in all conductors, and there are certain limits recognized and allowed by insurance companies as being sufficiently safe in order to avoid outbreak of fire in inflammable materials in close proximity to conductors—such as the wood casing which carries the electric wires. Further, if there is any tendency to heating, this may be kept down by good ventilation of air. Insulated conductors are not capable of such cooling, and lower limits are therefore set in such cases. In the case of a resistance which is situated so that it may be well ventilated, then the usual limits may be safely exceeded, especially where the current may be flowing for only a short time. Sufficient space between coils must be allowed for this cooling effect. Further, the wires may be backed by a sheet of asbestos to protect the wooden parts of the frame.

The following table (VIII.) shows the ordinarily allowable limits for wires of copper based on two standards, one at the rate of 1000 amperes per square inch in cross-section, and the other that adopted by the Institution of Electrical Engineers.

TABLE VIII.

CARRYING CAPACITY OF COPPER WIRES.

S.W.G.	Current at 1000 amps. per sq. in.	I.E.E. standard.
24	0.38	—
22	0.62	1.7
20	1.0	2.6
18	1.8	4.2
16	3.2	6.8
14	5.0	9.8
12	8.5	15.0

These figures, however, are given for wires which are insulated and enclosed in casing. Under such conditions there can be no cooling effect by ventilation, and in order to prevent an undue rise in temperature the current must be kept low. Where resistance wires are exposed and well ventilated and not in contact with inflammable materials, a very much higher limit may be set, but it must be remembered that as far as ordinary conductors are concerned the less their resistance the smaller will be the drop of volts along them, and the greater E.M.F. will be available for the work in hand.

Forms of Resistances.—Attention must now be directed to the most suitable forms of resistance frames or rheostats, and the most satisfactory methods of arranging the coils. Our aim is to attain certain conditions with a minimum of cost. Price of material is a consideration, and also its permanence in a corroding atmosphere, its resistance, the extent of variation of resistance possible, and the thinnest wires compatible with safety.

Choice of Wire.—For practical purposes iron and German silver are available. The latter has the greater resistance and is less liable to corrosion. Compared with iron it is expensive. Against the cheapness of the iron must be set its great liability to corrosion, and hence the production of

poor contacts unless protected from the atmosphere by varnish or lacquer. Iron wire has a specific resistance of $9.6 \text{ microhms per cm.}^3$ as against about 32 microhms for German silver. Hence for small resistances which are not required to carry large currents German silver is to be preferred, while for larger currents demanding much heavier wire, iron must be chosen on account of its cheapness. Such wire might be bought for about $4d.$ per lb. as against $2s. 6d.$ per lb. for German silver.

Coiling the Wire.—In order that much resistance can be obtained in a small compass, wires are best in the form of coils. In the case of short thin wires this can readily be done by hand by coiling round a cylinder of suitable diameter—small for thin wires and larger for thicker wires. If the wire is closely coiled the coils can subsequently be stretched to convenience. Heavier and stiffer wires can be readily coiled by winding round an iron rod or cylinder slowly rotating in a lathe. The end of the wire can be fastened to the chuck, and the wire can be stretched even by hand, so that the coil is produced by a taut wire and not a loose one. Long lengths of coil can thus be prepared and subsequently cut to more convenient sizes.

Types of Resistances.—

A most simple resistance might be made somewhat on the lines shown in Fig. 67, where A is a wooden framework, and B, B are the coils or a single coil opened out at intervals. The coil is fastened to the framework

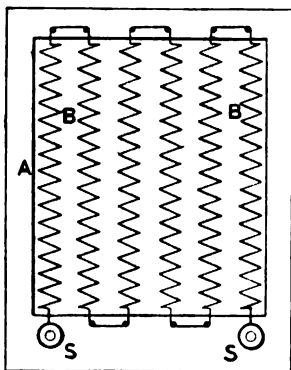


FIG. 67.—Simple resistance frame.

by screws, and the ends are joined to the terminal screws S, S, to which the connecting wires are attached. Such a simple form provides for no variation, and can only be cut

out by disconnecting and joining the wires. A cutting-out switch is shown to effect this in Fig. 68. Here the ends of the resistance coil are brought to brass blocks, C, C'. S, S are the terminal screws, one of which is connected to the block C and the other to the single arm of the switch. When the arm is on C' the resistance is in the circuit; when on C the resistance has been removed. Even in this case there is no provision for varying the resistance. Such variation may be made in the arrangement shown in Fig. 69. This shows the resistance divided into four parts, and wires brought from

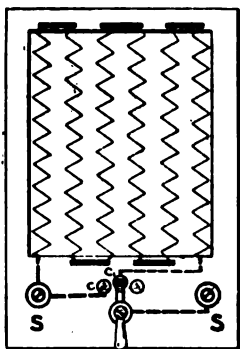


FIG. 68.—Simple resistance with cut-out.

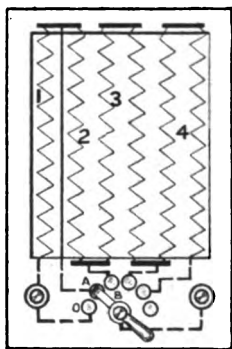


FIG. 69.—Variable resistance.

these divisions to brass or copper terminal blocks. These blocks are arranged on the arc of a circle in the centre of which the arm of the switch is pivoted. When the arm is on block O the resistance is not being used. When on A one coil is in use; on B, two coils, and so on. Variation of resistance is therefore produced by the number of coils. When all the coils are in the circuit the current is small; when only one coil is being used the current is larger. Coil 1 should, therefore, be capable of carrying more current than coil 4, and, indeed, the wire of the coils may conveniently vary in thickness, coil 1 being the thickest. In

coils 2, 3, and 4 the necessary resistance will thus be obtainable by shorter coils, and a saving of metal is thereby effected. But more than this is attained. When this method is adopted it becomes easier to vary the proportion of resistance in the different parts of the board. Thus the resistance of the separate parts should not be equal, but should more conveniently vary, coil 4 containing much more resistance than coil 1. Imagine a single piece of work in the vat, and the whole of the resistance in use. The addition of a similar piece of work practically cuts down the resistance of the bath to one half. But to supply twice the current for this increased area will demand a considerable reduction of resistance in the external circuit, and this is done on the board. Further additions of work make a less pronounced demand for current, and smaller variations of external resistance are required to attain this. This further advantage is therefore gained by the different diameters of wires, as shown in Fig. 70.

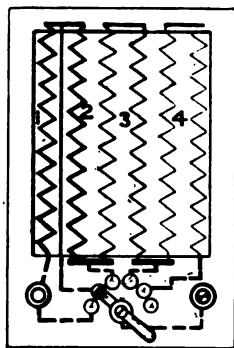


FIG. 70.—Variable resistance with wires of different diameter.

A simple arrangement dispensing with a switch is shown in Fig. 71. A, A are two wooden bars fastened together by long thin iron bolts with nuts to produce the necessary

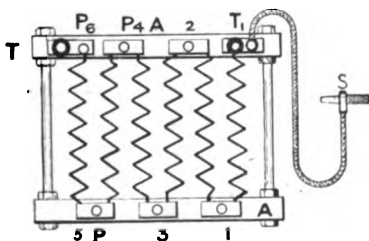


FIG. 71.—Variable resistance. Another form.

spacing. P, P, P are brass plates about $2'' \times 1'' \times \frac{1}{16}''$ to $\frac{1}{8}''$ thick, each having a slightly tapered hole. These plates are conveniently attached to the wooden base by screws, which also serve to firmly connect the coils. The arrangement will

be readily understood from the diagram. The terminal plates are provided with screws T and T_1 , to which connections are made. At T_1 a flexible lead of convenient length and carrying capacity terminates in a brass plug (S). When this plug is not in use all the resistance is in the circuit, and may now be taken out step by step by successively placing the plug in the holes in the order in which they are numbered.

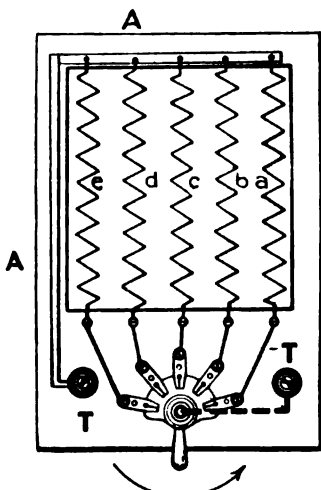


FIG. 72.—Parallel resistance.

This can be accomplished by arranging the coils in parallel. The idea is sketched in Fig. 72. To one terminal of this resistance, a thick strip of brass, AA , is attached. The five coils, a , b , c , d , and e , may be of the same thickness, and are connected to this brass or copper strip, the other end in each case terminating in a special end, shown in section in Fig. 73. The switch now consists, not of a single bar, but of a shaped piece of copper about $\frac{1}{16}$ inch thick, this being mounted and joined to the other terminal T . The resistance-board having been attached in the circuit, by moving

momentarily decreased, but this is not of much consequence where currents are only small. The arrangement, however, is easy to construct, and cheap, but great care must be taken that good connections are made at the ends of the coils, and this may be assured by soldering each contact.

Use of Wires in Parallel.

—A disadvantage of all the foregoing forms is the fact that in every case the heaviest currents have to be carried by single coils. A better plan would seem to utilize *all* the coils for carrying the heaviest currents.

the switch in the direction shown, the coil *a* of greatest resistance and least carrying capacity is introduced into the circuit. As the switch is moved a further stage, the coil *b* is also introduced into the circuit, but in parallel with *a*. Now, the resistance of two wires in parallel is less than either wire singly. The resistance being diminished, the current thus increased is not now carried by

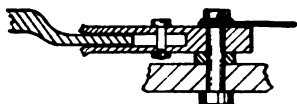


FIG. 73.—Details of switch.

a single wire, but by both wires. Similarly, when the five coils are in use, the resistance is reduced to a minimum, and the maximum current is being shared by all the coils, and the diameter of these may thus be kept down. If these coils are identical, then the variations of resistance are as follows :—

Least current	. . . with <i>a</i> or <i>e</i>		
Increasing current	. { <td>Maximum current</td> <td>. . . ,, <i>a, b, c, d, and e.</i></td>	Maximum current	. . . ,, <i>a, b, c, d, and e.</i>

If the coils are of different diameters, say, of increasing thickness from *a* to *e*, then we get more variations of resistance, viz. *a*; *a* and *b*; *a, b*, and *c*; *a, b, c*, and *d*; *a, b, c, d*, and *e*; *b, c, d*, and *e*; *c, d*, and *e*; *d* and *e*; and *e*. Thus nine different resistances are obtained from five coils.

A further modification, permitting the resistance to be cut out entirely, could be made by attaching a similar terminal to the strip *A*. With regard to such a parallel resistance it may be maintained that for heavy plating currents the idea of making all the coils share in carrying the current is a good one.

Other Forms of Resistances.—For smaller currents, say, up to 20 amperes, other forms of resistance, combining compactness and greater variability, are in common use. One of these is shown in Fig. 74. It consists of a number of

H

carbon plates about $\frac{1}{4}$ inch thick, supported on end in, but insulated by non-conducting strips from, an iron frame. The end plates are of metal, to which are attached binding screws. By means of a screw actuated by a small hand-wheel, the plates may be tightened or loosened, offering least resistance

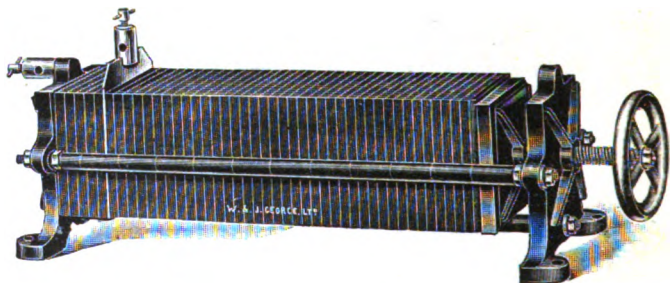


FIG. 74.—Carbon plate resistance.

when tight, and more when loose. The arrangement admits of variation of the resistance most gradually, without the jerks which occur when coils are used. To diminish the resistance still further, an additional metal plate can be inserted in any position in place of one of the carbon plates, and one connection made at this point by means of a similar binding

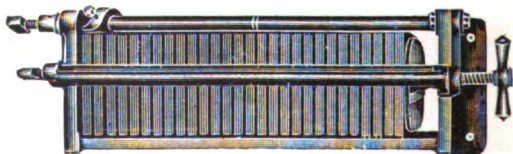


FIG. 75.—Carbon plate resistance. Wall pattern.

screw. Such resistances can be used singly or arranged in parts, so that the parts may be put in parallel, these arrangements offering greater limits of variation. A similar resistance for fastening to the wall is seen in Fig. 75.

Another very compact form of resistance for small work is shown in Fig. 76. It consists of a coil of wire—usually

of German silver or similar alloy—wound on a circular or rectangular slate base, and having suitable terminals. The base is first grooved in the form of a long spiral, so that the wire coils lie very close together without any chance of touching. When the two terminals are used, the whole of the resistance is in the circuit. Variation may now be

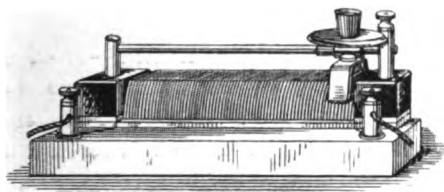


FIG. 76.—Compact resistance wound on slate base.

obtained by means of the sliding contact which travels along the rod of circular, or preferably for greater rigidity, triangular section. In using this, one connecting wire should be transferred from the bottom to the top terminal. Such a resistance is open to considerable variation, may be allowed to rise in temperature considerably without fear of injury, and is, moreover, inexpensive.

CHAPTER VII

Measuring Instruments

Necessity for Measuring Current.—From the point of view of economy alone, any material or power which costs money should be accurately measured. In some electro-metallurgical works, the electric power is an item of considerable importance on the annual balance-sheet, and the same care should be exercised in its use as would be taken, say, with gas from a public company. Still more important, however, is the desirability, nay, the necessity, for uniform working—of knowing with fair accuracy the current passing through a bath. It is the current which determines the rate at which the metal is deposited, and this in turn determines the character of the deposit. Hence the necessity for some forms of instruments which automatically record the current passing through the bath. In these days of cheap and reliable instruments there should be no need whatever to adopt such unfortunate and outrageous methods of judging the current by sparking with a stout wire on the anode and cathode bars. Nor even is the quality of the deposit a reliable guide of the current. Thus in two baths differing in composition the same current on the same area of cathode surface may produce two totally different kinds of deposit. Still further, one of the easiest methods of judging the condition of a solution is the comparison of the ammeter and voltmeter readings. Thus in an arrangement shown in Fig. 49 (p. 59), V shows the E.M.F. absorbed in the bath in maintaining the current shown on the ammeter A. Now, according to Ohm's law—

$$C = \frac{E}{R} \text{ and } R = \frac{E}{C}$$

that is, the resistance (in ohms) of the bath is found by dividing the current (amperes) into the E.M.F. (volts) absorbed in the bath. This E.M.F. is, as has already been shown, approximately constant for the same current density. When through certain circumstances which may often occur—for example, lack of metal, cyanide, or acid, or too low a temperature—the resistance of the bath is increased, this is at once shown by a comparison of the ammeter and voltmeter readings, and the error can be at once rectified. The necessity of such current and P.D. recorders is apparent.

Principles of Recorders.—Now, current must be measured by—shall we say—what it does. The most obvious effects of the electric current are—

(1) **Chemical Effect**, whereby chemical substances are decomposed by the passage of the current through them, when measurable products are obtained. This principle, however, would be absolutely useless unless the effect can be exactly reproduced over and over again. Thus, 1 ampere in one hour deposits 1.182 gram of copper from the sulphate solution, but not from the cyanide solution. With a very weak solution the ampere hour would deposit less copper, and therefore the method would be unreliable apart from its being exactly reproducible. How this is assured will be subsequently seen, but an arrangement for determining the strength of the current by this chemical effect is called a **voltameter**. Some forms will be described.

(2) **The Magnetic Effect.**—It is well known that a current flowing in the vicinity of a freely suspended magnetic needle causes a deflection of the needle, the direction and amount depending upon the strength of the current, its direction, and the distance of the current from the needle. Thus in Fig. 77 NS represents a freely suspended magnetic needle, pointing north and south. The wire AB carries a current in the direction shown. The needle is then deflected so that its north pole points in a more westerly direction. If the wire is now brought beneath the needle the deflection is in the

opposite direction. Reversal of the direction of the current reverses the deflection. Similar effects are observed when

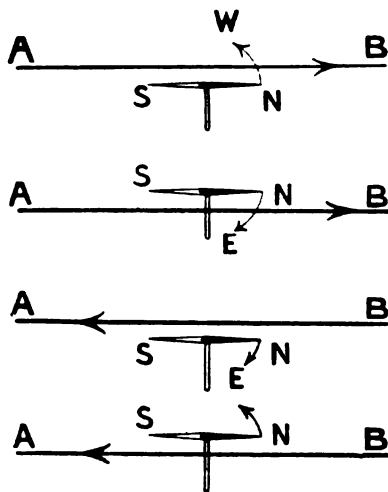


FIG. 77.—Effect of electric current on magnetic needle.

the wire is held vertically, as shown in Fig. 78, or if it takes the form of a coil, as shown in Fig. 79. The amount of the deflection depends upon the current and the distance of the wire or coil from the

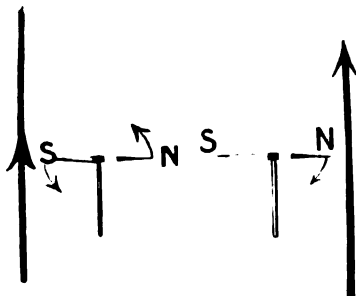


FIG. 78.—Effect of electric current on magnetic needle. Wires vertical.

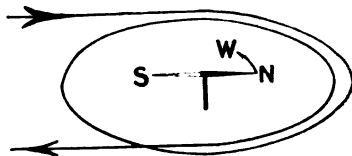


FIG. 79.—Effect of current in a coil.

needle. Instruments employing this principle are called **galvanometers**, but while extensively used in some branches

of electrical measurement, do not find their way into electroplating workshops.

Again, in Fig. 80, if a current is passed through a coil of wire, AB (called a solenoid), which surrounds an iron rod, P, the rod becomes magnetized, and if hung only partly in the coil, is drawn more completely into it. The force with which the iron rod is sucked into the coil depends upon the current and the number of turns in the solenoid. Then in Fig. 80 it will be seen that the movement of the iron rod can easily be recorded by a pointer E attached to the end and passing over

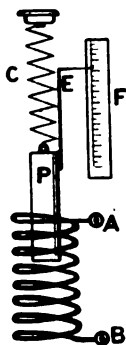


FIG. 80.—Current in a solenoid.

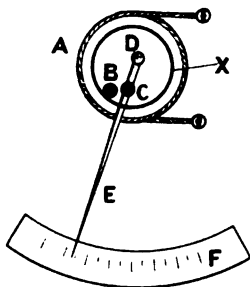


FIG. 81.—Principle of simple "gravity" ammeter.

a scale F, the iron rod being supported to allow of vertical movement by a light spring C. Instruments for measuring current can be made on this principle.

Again, if a current is sent through a coil of wire containing two pieces of soft iron they become similarly magnetized, and, according to the well-known law, repel one another. By fixing one piece of iron the movement of the other can be magnified, and by means of a pointer and scale quantitatively recorded. The arrangement is shown in Fig. 81, where A is the coil of wire, B is a piece of soft iron fixed relatively to the coil, while C, a similar piece of iron, is capable of

movement, being supported at the pivot D with a light pointer E attached, the end of which passes over a graduated scale F. This principle is largely employed in instruments called **ammeters** and **voltmeters**.

(3) **Heating Effect of Current.**—When passed through a wire of appreciable resistance the electric current generates heat. This may be (1) transferred to water, and the current can be deduced by the amount of heat developed, but this principle is not applied in workshop instruments; or (2) allowed to expand the wire. The amount of expansion is a measure of the heat, which in turn depends upon the current. A simple form of apparatus showing this is depicted in Fig. 82.

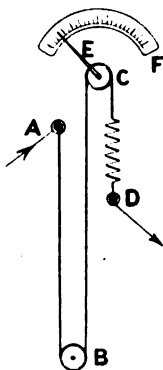


FIG. 82. — Current shown by its heating effect.

ABC is an iron, German silver, or other high resistance wire fixed at A and passing over moving pulleys at B and C. The wire may be kept taut by either a weight or spring attached at D. When a current passes, the heat produced expands the wire, and this causes a movement of the pulley which can be magnified by a long pointer E passing over the scale F. This principle is employed in one form of instrument, but does not find its way into the workshop.

Hence it will be seen that many methods of measuring and recording the current are available, and attention must now be given to some of those principles which find application in instruments of practical importance.

Voltmeters.

The Gas Voltmeter.—When a current is passed through weak sulphuric acid between platinum plates, oxygen and hydrogen are evolved. If these plates are close together and covered by one tube, the mixed gases are collected.

This is shown in Fig. 83. If separate tubes are employed, as in Fig. 84, the gases are collected separately, when the volumes of oxygen and hydrogen are in the proportion of 1 : 2. Now, it is shown (on p. 126) that 1 ampere in one minute produces 6.93 c.c. of hydrogen, at N.T. and P.,¹ and at the same time one-half of this amount, viz. 3.47 c.c. of oxygen, is evolved at the anode. If the two gases are collected

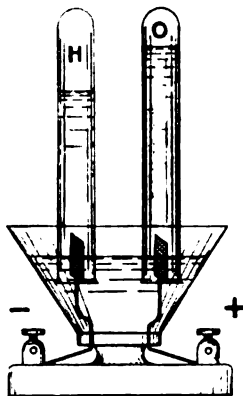
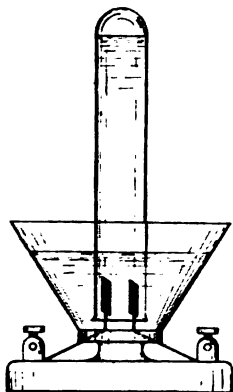


FIG. 83.—“Mixed gas” voltmeter. FIG. 84.—Voltmeter for separate gases.

together this would mean a total volume of 10.4 c.c. If now we insert this in our circuit the current will be indicated by the volume of gas produced in a given time. Thus if 15.8 c.c. are evolved in one minute, then the current is $\frac{15.8}{10.4} = 1.52$ amperes. While not actually used in a workshop, the idea is often used in more purely scientific work. But notice its disadvantages :—

(1) If the voltmeter is put into a circuit its resistance at once diminishes the current, and hence this is less with, than without, the voltmeter in the circuit.

¹ N.T. and P. means normal temperature and pressure, or 0° C. and 760 mm. Hg.

(2) Even if the instrument were permanently in the circuit it would be wasteful, for it absorbs at least $2\frac{1}{2}$ volts even if well constructed, and this might even exceed the volts used in the bath.

(3) It does not record the exact current at any given moment. When the volume of gas has been measured and the current calculated, only the **average current** during the experiment is given.

The Copper Voltameter.—Instead of the gas voltmeter we might insert in the circuit a small copper bath. By using a weighed cathode, the amount of copper deposited in a given time may be easily determined by weighing the plate a second time. Thus if in 20 minutes 5.44 grams of copper are deposited, then the current is calculated as follows:—

1.182 gm. Cu in 1 hour by 1 ampere

1 gm. " " $\frac{1}{1.182}$ ampere

5.44 gms. " " $\frac{5.44}{1.182}$ "

5.44 " " 1 min. by $\frac{5.44 \times 60}{1.182}$ amperes

5.44 " " 20 " $\frac{5.44 \times 60}{1.182 \times 20}$ "

$$\therefore C = \frac{5.44}{1.182} \times \frac{60}{20} = 13.8 \text{ amperes}$$

or more generally—

$$C \text{ (amperes)} = \frac{\text{copper deposited (gms.)}}{1.182} \times \frac{60}{\text{minutes}}$$

Such an arrangement is called a copper voltameter, and may be extensively used, more especially for experimental work. It is very reliable if a few conditions are observed. These are—

- (1) Careful weighing of plates and timing of experiment.
- (2) Strong electrolyte.

(3) Only a moderate current density not exceeding 10 amperes per foot of cathode surface.

For workshop purposes it would present the following disadvantages :—

(1) If introduced into a circuit it would add resistance, absorb E.M.F., and alter the current.

(2) For practical purposes its plates would need to be very large.

(3) As much copper would be deposited in the voltameter as in the bath.

Further, only the *average* current would be given by this method. For small experimental work such voltameters are extremely useful, in that they add up all the coulombs which pass through the circuit. Thus, in the example above, where 5.44 grams of copper were deposited, the number of coulombs would be—

$$\frac{\text{weight copper deposited}}{\text{weight copper deposited by 1 coulomb}} = \frac{5.44}{0.000329} = 16530$$

which are equal to $\frac{16530}{3600} = 4.59$ ampere-hours.

The Silver Voltameter is more accurate than the copper voltameter, and is used for the very accurate checking of measuring instruments, to be afterwards described.

Ammeters which are almost entirely used in electro-plating workshops are of simple construction. Fig. 81 shows the essential parts.

X is a brass cylinder on which is wound a coil, A, the ends of the coil being joined to the two terminals. Fixed to this cylinder is a short, thin rod of iron, B. C is a similar piece of iron which, when no current passes through the instrument, is close to, but not quite touching, B. It is fixed to swing about D as centre, and the pointer attached on the opposite side magnifies the motion. The pointer moves over a scale on the dial. When a current is passed, the two iron rods, becoming magnetized, repel one another, and C being movable swings

about D as centre, and a deflection is obtained. The amount of the motion depends upon the current, the number of turns of wire constituting the coil, and the diameter of the coil. The further the rods separate the less is their repulsion, and in order to maintain the movement and produce an even scale the iron pieces need careful adjustment, so that as one effect fails, another comes into greater prominence. Unless made exactly to a pattern, each instrument would require its own scale. This would be prepared by sending known currents through the instrument and marking the deflections produced. Usually, however, a large number would be made to a single pattern, and sufficient accuracy would thereby be attained for ordinary purposes. These instruments may be obtained for wide ranges of current at a cost of from £1 to £2. They are graduated somewhat on the following lines :—

10 amperes—from 1, 1 ampere being the first reading.

50 amperes would have a first reading of 5 amperes, but graduations different from these might be put on. Usually the scale is not exactly uniform, but so long as the instrument is made to pattern and the correctly graduated scale carefully put on, this does not matter.

Calibration of an Ammeter.—The accuracy of the instrument may always be checked by a method which is available in any workshop, provided that a fairly accurate balance is at hand. For this purpose arrange a small copper bath with strong acidulated sulphate solution, and with a copper anode and a thin but large copper cathode. Fit it up to a resistance (variable) and the ammeter, and join up to a source of current which is as constant as possible. Send a current for a short time, and adjust it so that the current density does not exceed 10 amperes per square foot. Remove cathode, rinse well, and carefully dry. This may be done by finally rinsing with distilled water and drying in an air or water oven or even holding well over a Bunsen flame. When cool, carefully weigh. Replace in the copper voltameter and switch on the current, noting the time at which the current is started.

Carefully observe ammeter reading and maintain this constant by slightly altering the resistance if necessary. Allow current to flow until from 1-2 grams of copper have been deposited. Discontinue current, again observing time. Remove cathode plate. Well rinse, dry, and reweigh. From the weight of copper deposited and the time of deposition the average current is calculated.

Example.

Reading on ammeter = 3.25
 Weight of cathode before deposition = 14.175 grams
 " " after " = 15.451 "
 Weight of copper deposited = $\frac{1.276}{1.182}$ gram
 Time current started = 10.20
 " " stopped = 10.40
 Current flowed $\frac{20}{1}$ minutes

Then—

$$C \text{ (amperes)} = \frac{\text{weight copper deposited}}{1.182} \times \frac{60}{\text{minutes}}$$

$$C = \frac{1.276}{1.182} \times \frac{60}{20} = 3.23 \text{ amperes.}$$

This difference of the calculated from the observed current is slight, and could reasonably be neglected. Where wider differences occurred, other similar experiments would be made with varying currents, and any errors found—which may or may not be uniform—can subsequently be allowed for.

Increasing the Range of an Ammeter.—The desirability of increasing the range of an ammeter is at once obvious. Where the work in a vat varies considerably the current required must vary in the same ratio. Yet it would be quite unusual for an ammeter to range from 1 ampere to 50 amperes. If such graduations were on the scale they must necessarily be so crowded in some parts that reading becomes impossible. We need to enlarge the scale or divide it into two or more parts, as is done, for example, in the Twaddell hydrometer.

For a range of 0-25 amperes a suitable division of the scale would be as follows (Fig. 85) :—

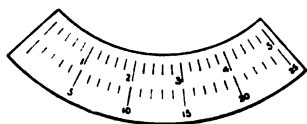


FIG. 85.—Scale for two-range ammeter.

Scale A, from 0-5 by tenths.

„ B, „ 0-25 by units.

It is, however, the part of the ammeter which controls the movement of the needle which needs altering, and this can be done in several ways.

(1) **Two Separate Coils** placed one over the other. One coil should then be of few turns and thick wire, the thick wire to carry the heavier current, and the few turns will suffice to give a convenient deflection. The other coil might be of somewhat thinner wire, but to consist of a larger number of turns. It is simply a matter of adjusting the number of turns, etc., in each circuit to make the readings suitable for each scale.

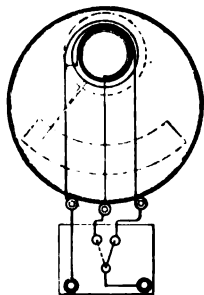


FIG. 86.—Ammeter with two windings and switch.

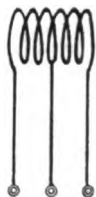


FIG. 87.—Divided coil for two-range ammeter.

Such an instrument would need a switch, as shown in Fig. 86, the switch being arranged so that the coil with a few turns would be first put in, and when it was certain that the current was low enough (5 amperes or less), the coil with the larger number of turns could be inserted. Such a two-range instrument is of great use.

(2) **A Divided Single Coil** might be used as shown in

Fig. 87. The side view of the coil is shown (the coil being stretched out to show the connections better), one end of the coil forming one terminal of the instrument, and the two other terminals being controlled by a switch as before.

(3) **By Shunts.**—A shunt is a coil or strip connected across the terminals of an ammeter, to the resistance of which it bears a fixed ratio. Thus in Fig. 88 a shunt coil is shown at A.

Now, if this shunt coil has exactly the same resistance as the instrument, then on connecting up the ammeter at x, x or y, y , one-half of the current will pass through the instrument, and one-half through the shunt. If the current in the circuit is 10 amperes, then 5 amperes pass through the shunt and 5 amperes through the instrument, and deflect the needle. Such a deflection should now be marked 10, and all the other readings should be doubled while the shunt is in use. The maximum reading of the instrument is thus doubled. But the shunt may have another ratio. Thus if it has $\frac{1}{9}$ the resistance of the instrument, then it will convey 9 times as much current as the ammeter, so that the latter carries only $\frac{1}{10}$ of the current in the circuit, and the range is thereby increased 10 times. Moreover, the shunt can be arranged so that it may be put out of action by a simple switch, and where this happens the instrument may be used first over its ordinary range, and then, by inserting the shunt, its range can be increased and the readings on the instrument either multiplied up or an additional scale marked upon the dial.

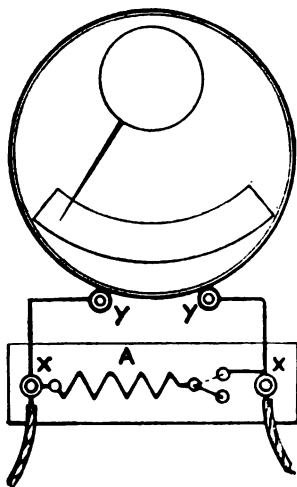


FIG. 88.—Ammeter with shunt.

Voltmeters may be constructed on exactly the same principle as ammeters, but with this great difference. In an ammeter, which is placed directly in a circuit, the resistance must be low, and this condition is attained by a coil of thick wire with only a few turns. An examination of a voltmeter would reveal the fact that the coil is of many turns of thin wire. The reason for this will now be explained. The object of the voltmeter is to measure the difference of potential between any two points in a circuit. From the plater's point of view these two points are either the generator terminals, or more usually the bath terminals. In the latter case, the reading in volts is the E.M.F. being used in driving electricity through the bath, and this at once gives an idea of the condition of the solution. The voltmeter is arranged as shown in Fig. 49. *a* and *b* represent the anode and cathode, A the ammeter and V the voltmeter. While the ammeter is placed directly in the circuit the *voltmeter is placed as a shunt* across the bath. At the point *a* the current has two paths—one through the bath, and the other through the voltmeter. In order that the proportion of current passing through the voltmeter shall be small, the instrument is of high resistance, this being obtained by a coil of thin wire of many turns, the many turns being required to multiply up the effect of the small current. We may next inquire why, if a current produces the deflection, the reading is given in volts. Imagine the instrument to have a resistance of 100 ohms. If its terminals are placed upon two points, the P.D. between which is 1 volt, then the current produced in the instrument will be—

$$C = \frac{E}{R} = \frac{1}{100} \text{ ampere}$$

This small current produces a reading which is marked 1 volt. Again, when placed across a P.D. of 5 volts, the current generated in the instrument is—

$$C = \frac{E}{R} = \frac{5}{100} = \frac{1}{20} \text{ ampere.}$$

This produces a larger deflection, which is now marked 5 volts, and so on. If subsequently the terminals are connected to two points in a circuit and a reading of 5 volts is obtained, then the current producing that deflection is $\frac{1}{20}$ ampere, which has been produced by a P.D. of 5 volts acting on the voltmeter resistance of 100 ohms. This would apply whether the resistance of the voltmeter were low or high. The necessity for its being high will now be made clear. The voltmeter being arranged as a shunt across the bath, whatever current passes through the voltmeter is, as it were, taken from the vat. Hence the ammeter reading is in excess of the current in the bath, by the amount which passes through the voltmeter. If the voltmeter is a good conductor, that is, has little resistance, then greater facility is provided for the current to pass between the two points *a* and *b*, and hence while the voltmeter is "on," the P.D. between the two points is lowered and an exact record of its value before the voltmeter was applied is not obtained. Hence the higher the resistance of the voltmeter, the smaller the alteration produced when it is applied over any part of the circuit, and greater accuracy is obtained. In a cheap instrument for workshop practice the resistance may be about 30-50 ohms, but this is very large as compared with that of a large bath filled with work, for here the resistance should be very small indeed.

CHAPTER VIII

Quantitative Electro-deposition

The Different Rates at which Metals are deposited.—

The control of the actual weight of metal deposited is often a matter of importance. In the deposition of gold on fine wires, for example, a little excess of gold may soon make a great difference to the financial side of the process, when this excess is not known. Again, it may be observed that with different metals their rates of deposition are distinctly different, and even with the same metal, the rates of deposition from two different solutions may differ. Thus, copper is usually deposited from a cyanide solution at twice the rate at which it appears from the sulphate bath, while gold comes out from the chloride solution at only one-third of the rate at which it is deposited from the cyanide solution commonly used for gilding. Yet while these amounts are so different, they are none the less definite, and these definite values for each of the more common metals will now be traced. It is, however, possible, that in attempts made to ascertain these values by experiment, the definite values might not be readily observed, not due necessarily to inaccurate working, but more probably due to failure to realize the best conditions for obtaining these values. Let it then be first stated that for each metal there is a certain maximum which may be deposited per ampere-hour, and which cannot possibly be exceeded, but which, owing to failure to realize the best conditions, may not be nearly attained.

The Ampere.—By the term **current** we understand

the *rate at which electricity flows* round a circuit. Speaking of water, we should express its rate of flow in a pipe in terms of gallons per minute, or cubic feet per hour, in each case the quantity in a unit of time, and we have a choice of units, both of quantity of water and time. Similarly current is expressed in terms of quantity of electricity and time. The unit of quantity of electricity is the **coulomb**, which is the amount of electricity required to deposit 0.001118 gram silver. The unit of time selected is the second. Unit current or rate of flow (the ampere) is that obtained when unit quantity (the coulomb) passes any given point in the circuit in unit time (one second). Hence the ampere is defined as the steady current which deposits 0.001118 gram of silver per second or $0.001118 \times 3600 = 4.025$ grams silver per hour.

Faraday's Laws.—Now, the different rates of deposition of the metals were most carefully investigated by Michael Faraday, who, as the result of a series of experiments, enunciated the following laws which bear his name:—

Law No. 1.—That the amount of deposit is proportional to the time, *i.e.* that the same current will deposit twice as much metal in two hours as in one hour.

Law No. 2.—That the amount of deposit is proportional to the current, *i.e.* that in the same time, 10 amperes will deposit under ideal conditions ten times as much metal as 1 ampere.

Law No. 3.—That the amount of metal deposited is proportional to its chemical equivalent. This is *the* important law, and must be explained in detail.

Chemical Equivalents are *chemically equal* quantities. For example, 1 gram of hydrogen combines with 8 grams of oxygen. Taking hydrogen as the standard ($= 1$), the equivalent of oxygen is 8. Again, 8 parts by weight of oxygen combine with 12 parts by weight of magnesium, that is, 12 parts of magnesium are *chemically equal* to 1 part by weight of hydrogen in that they both combine with the same weight of oxygen—viz. 8 parts. Chemical equivalents are thus the amounts of

the elements which will combine with or replace unit weight of hydrogen. They are also the weights which combine with one another. These equivalents are obtained by experiment. Thus 32.5 grams zinc turn out (a) 1 gram of hydrogen from sulphuric acid, (b) 31.8 grams copper from copper sulphate, (c) 108 grams of silver from silver nitrate, (d) 65.7 grams of gold from gold chloride, (e) 59 grams of tin from stannous chloride, and (f) 100 grams of mercury from a mercuric compound. Similarly 32.5 grams of zinc combine with (a) 8 grams oxygen, (b) 16 grams sulphur, (c) 35.5 grams chlorine, and so on. From experiments carried out on these lines the following table can be compiled:—

TABLE IX.
CHEMICAL AND ELECTRO-CHEMICAL EQUIVALENTS.

Element.	Chemical equivalent.	Grams deposited per ampere-sec. (E.C.E.)	Grams deposited per ampere-hour.
Aluminium	9.0	0.0000931	0.334
Chlorine	35.5	0.000367	1.321
Copper (cupric) . .	31.8	0.000329	1.182
Copper (cuprous) .	63.6	0.000659	2.364
Gold (aurous) . . .	197.0	0.00204	7.35
Gold (auric) . . .	65.7	0.00068	2.44
Hydrogen	1.0	0.00001035	0.0373
Iodine	127.0	0.001315	4.734
Iron	28.0	0.00029	1.04
Lead	103.5	0.00107	3.87
Mercury (mercuric) .	100.0	0.001035	3.72
Mercury (mercurous)	200.0	0.002070	7.45
Nickel	29.35	0.000302	1.085
Oxygen	8.0	0.0000828	0.298
Silver	108.0	0.001118	4.025
Tin (stannic) . . .	29.5	0.000305	1.095
Tin (stannous) . .	59.0	0.000610	2.19
Zinc	32.5	0.000336	1.21

The chemical equivalent is first a matter of chemical analysis, though this may sometimes be carried out by quite simple experiments. In the next column we start with the figure for silver or that for hydrogen. The ampere is

defined as the steady current which deposits under the best conditions 0.001118 gram of silver per second. With unit current (the ampere) the amount of electricity which passes through the solution in each second is called the coulomb. Hence 1 coulomb = 1 ampere-second, and, generally—

$$\text{Coulombs} = \text{amperes} \times \text{seconds.}$$

Thus—

$$1 \text{ ampere-hour} = 1 \times 3600 = 3600 \text{ coulombs.}$$

amp. secs.

Now the amount of the element deposited by 1 coulomb is called the **electro-chemical equivalent** (E.C.E.), and these E.C.E.'s in column 3 of the above table are obtained from the silver value by simple proportion. Thus from the E.C.E. of silver we calculate that for copper(ic)—

$$\begin{aligned} 108 \text{ parts by weight Ag} &\equiv 31.8 \text{ parts by weight Cu(ic)} \\ \therefore 1 \text{ part } & \text{,, } \text{,, } \equiv \frac{31.8}{108} \text{ } \text{,, } \text{,, } \text{,,} \\ \therefore 0.001118 \text{ gram Ag} &\equiv \frac{31.8 \times 0.001118}{108} \text{ gram Cu(ic)} \\ &= 0.000329 \text{ gram copper} \end{aligned}$$

Then the figures in column 4 are obtained by multiplying those in column 3 by 3600 (seconds in one hour). We have thus the maximum amounts of these metals which can be deposited by one ampere-hour. They are obtainable only under the very best conditions, conditions which are not always realized in plating solutions. From these figures we can calculate the weight of deposit for any given current and time, thus—

Calculate weight of nickel deposited by 24 amperes in $4\frac{1}{2}$ hours.

Now 1 ampere in 1 hour deposits 1.085 gram nickel

\therefore 24 amperes in 1 hour deposit 1.085×24 gram nickel

and 24 ,, $4\frac{1}{2}$ hours ,, $1.085 \times 24 \times 4\frac{1}{2}$ gram nickel

$$\text{Weight of nickel} = \frac{1.085 \times 24 \times 9}{2} = 117.2 \text{ grams}$$

It must be remembered that this is the maximum amount of metal which could be deposited, under the best conditions. Such an amount would not ordinarily be obtained in practice. Again—

Calculate current required to deposit 1 ton of copper in 24 hours.

$$1 \text{ ton} = 2240 \text{ lbs.} = 2240 \times 454 \text{ grams.}$$

Now, to deposit—

1.182 grams Cu in 1 hour requires 1 ampere

$$\therefore 1.182 \text{ ,, ,, 24 hours requires } \frac{1}{24} \text{ ,,}$$

$$1 \text{ gram ,, 24 ,, ,, } \frac{1}{24 \times 1.182} \text{ amp.}$$

$$\therefore 2240 \times 454 \text{ grams ,, 24 ,, ,, } \frac{2240 \times 454}{24 \times 1.182} \text{ ,,}$$

$$= 35,848 \text{ amperes}$$

This perhaps seems a large and almost unmanageable current, but while in some works deposition is carried out on such a scale, a smaller current would be used and passed through a number of baths *in series*. Thus—

35,848 amperes passed through 1 bath

or 3584.8 ,, ,, ,, 10 baths

or 358.48 ,, ,, ,, 100 baths

would yield the same total weight of copper. Again—

How long will it take to deposit 2 lbs. of copper by a current of 10 amperes?

Now, 1.182 gms. copper are deposited by 1 amp. in 1 hour

$$\therefore 1 \text{ gram copper is deposited by 1 ,, } \frac{1}{1.182} \text{ hour}$$

$$\therefore 2 \times 454 \text{ gms. copper are deposited by 1 ,, } \frac{2 \times 454}{1.182} \text{ hours}$$

$$\text{and } 2 \times 454 \text{ ,, ,, ,, 10 ,, } \frac{2 \times 454}{1.182 \times 10} \text{ ,,}$$

$$= 76.8 \text{ hours.}$$

The student should further exercise himself in these simple calculations, taking those which are of workshop interest.

Comparison of Weights of Two Different Deposits in the Same Circuit.—If a silver and acid copper bath are used in the same circuit, then under the best conditions, the metals are deposited in the proportion of their chemical equivalents, that is, for every 31·8 parts by weight of copper from the acid bath, there should be 108 parts by weight of silver.

Example.—What weight of silver (ozs. troy) will be deposited in a circuit in which 2 ozs. (av.) of copper are deposited.

Now, for 31·8 Cu there should be 108 Ag

$$\therefore \text{for 1 oz. (av.) Cu there should be } \frac{108}{31\cdot8} \text{ ozs. (av.) Ag}$$

$$\therefore \text{for 2 ozs. } \quad \quad \quad \quad \quad \quad \quad \frac{108 \times 2}{31\cdot8} \text{ ozs. (av.) Ag}$$

$$\text{But } 1 \text{ oz. (av.)} = 437\frac{1}{2} \text{ grains}$$

$$\text{and } 1 \text{ oz. (troy)} = 480 \text{ grains}$$

$$\therefore 1 \text{ oz. (av.)} = \frac{437\frac{1}{2}}{480} \text{ ozs. (troy)}$$

$$\begin{aligned} \therefore \frac{2 \times 108}{31\cdot8} \text{ ozs. (av.)} &= \frac{2 \times 108}{31\cdot8} \times \frac{437\cdot5}{480} \text{ ozs. (troy)} \\ &= 6\cdot2 \text{ ounces (troy) silver} \end{aligned}$$

Examples of this kind might easily be multiplied.

Copper and Nickel.—According to equivalents, 31·8 parts by weight of copper are deposited from the acid bath in the same time and by the same current as 29·3 parts by weight of nickel.

Example.—If the two baths are in series, what weight of nickel would be deposited (under the very best conditions) while 50 grams of copper appeared?

Then —

$$\begin{aligned}
 31.8 \text{ Cu} &\equiv 29.3 \text{ nickel} \\
 1 \text{ gram copper} &\equiv \frac{29.3}{31.8} \text{ gram nickel} \\
 50 \text{ grams copper} &\equiv \frac{29.3 \times 50}{31.8} \text{ grams nickel} \\
 &= 46.1 \text{ grams}
 \end{aligned}$$

This means that not only should 46.1 grams of nickel appear at the cathode, but a like quantity should disappear from the anode. This point is of prime workshop importance, and is dealt with further on in this chapter.

Calculation of Thickness of Deposits.—From the amount of metal deposited it will be easy to calculate the thickness of the deposit. Assume again that the metals are deposited exactly in accordance with Faraday's law. If on 1 sq. ft. of cathode surface we pass a current of 10 amperes, then copper, silver, and gold, for example, would be deposited in the proportion of 31.8 : 108 : 197 (Au from cyanide solution). Next, if these metals had the same specific gravity, that is, if equal weights of the metals occupied equal volumes, then these equivalent weights spread over equal areas would produce deposits of proportionate thickness. But this is not so. The specific gravities of the three metals are: Cu, 8.9; Ag, 10.5; Au, 19.5. The higher the specific gravity, the less is the volume occupied by a given mass. The volumes occupied by the chemical equivalents (in grams) are—

$$\text{Copper} = \frac{31.8}{8.9} = 3.58 \text{ c.c.}$$

$$\text{Silver} = \frac{108}{10.5} = 10.3 \text{ c.c.}$$

$$\text{Gold} = \frac{197}{19.5} = 10.1 \text{ c.c.}$$

Now, 26.8 ampere-hours deposit the gram equivalent, and therefore deposit 3.58 c.c. Cu, 10.3 c.c. Ag, and 10.1 c.c. Au,

or in the proportion of 1 Cu : 2.88 Ag : 2.82 Au. If spread over the same area the thicknesses of the layers produced would have the same proportion, and therefore if deposited quantitatively the same current density yields deposits of silver and gold nearly three times as thick as that of copper from the acid bath.

Thickness of Copper Deposits.—Assume a C.D. of 40 amperes per sq. ft. Calculate thickness of a one-hour deposit.

Total copper deposited = $40 \times 1.182 = 47.3$ grams.

Representing thickness of deposit as t ", we have—

Volume of deposit = $12 \times 12 \times t = 144t$ cu. ins.

1 cu. inch = 16.4 c.c.

1 c.c. copper weighs 8.9 grams

\therefore 1 cu. inch copper weighs $16.4 \times 8.9 = 146$ grams

\therefore $144t$ cu. ins. weigh $146 \times 144 \times t = 21,000t$ grams

Hence $21,000t = 47.3$

$$t = \frac{47.3}{21,000} = 0.00225 \text{ inch}$$

Similarly a C.D. of 10 amperes per sq. ft. would give a thickness of $\frac{1}{4} \times 0.00225 = 0.000562$ inch per hour, and to produce a thickness of 1 inch per hour we should require a current density of—

$$\frac{1}{0.000562} \times 10 = 17,700 \text{ amperes per sq. ft.}$$

The figure is of course outside the range of practicability, but from it more useful figures can be obtained. Thus *in one hour*—

177 (nearly 180) amperes per sq. ft. give $\frac{1}{100}$ " thick

17.7 (nearly 18) " " " $\frac{1}{1000}$ " "

while in 10 hours—

177 amperes per sq. ft. gives $\frac{1}{10}$ " thick

and 17.7 " " " $\frac{1}{100}$ " "

An approximate idea of the thickness of a deposit can therefore be readily obtained.

Example.—What thickness of deposit would be produced by 25 amperes per sq. ft. in 5 hours in an acid copper bath?

Now, 177 amperes per sq. ft. give $\frac{1}{100}$ " thick in 1 hour, and 177 amperes per sq. ft. therefore produce $\frac{5}{100}$ " thick in 5 hours,

$$\therefore 25 \text{ amperes per sq. ft. produce } \frac{5}{100} \times \frac{25}{177} = 0.00707"$$

or about $\frac{1}{140}$ " thick in 5 hours.

Further, from the weight of a deposit and the time in which it is produced we can calculate the current density used. Thus, a deposit of copper measures 3" \times 2" and weighs 3.5 grams. It was produced in 15 minutes. Calculate current density.

Now—

$$3.5 \text{ grams in 15 minutes} = 14 \text{ grams per hour}$$

$$14 \text{ grams per hour} = \frac{14}{1.182} = 11.85 \text{ amperes}$$

$$\text{Hence current on } 3" \times 2" = 6 \text{ sq. ins.} = 11.85 \text{ amperes}$$

$$\therefore \quad \quad \quad 1 \text{ sq. ft.} = 144 \text{ sq. ins.} = \frac{11.85 \times 144}{6} \\ = 285 \text{ amperes}$$

Similar calculations may be made for other metals, but these will have served to show the principles.

Anode and Cathode Efficiencies.—It has already been pointed out that only under the best conditions the full weight of metal can be obtained. Seldom, if ever, are these ideal conditions attained in workshop practice. In the nickel bath, for example, the amount of metal which should be deposited and dissolved can be calculated from the current and time. The appearance of gas, freely evolved at the anode, and perhaps only slowly at the cathode, is a sign that deposition is not proceeding as it might or ought. The following figures will serve to show the relative amounts of anode dissolved and metal deposited in an ordinary nickel plating solution using (a) a rolled anode, and (b) a cast anode.

I. ROLLED ANODE.

	Copper bath	Nickel bath.	
	Cathode.	Anode.	Cathode.
	Grams.	Grams.	Grams.
Weight of plate before experiment	30.372	30.890	22.285
" " after "	30.940	30.860	22.781
	0.568	0.030	0.496

II. CAST ANODE.

(a) *Rough.*

Weight of plate before experiment	30.940	129.808	22.780
" " after "	31.860	129.021	23.551
	0.920	0.787	0.771

(b) *Smooth.*

Weight of plate before experiment	31.860	126.591	23.491
" " after "	32.474	126.286	24.020
	0.614	0.305	0.529

These figures are from actual experiment, and show first by mere inspection that—

(1) In both cases the nickel deposits fall somewhat short of those which would be anticipated.

(2) That the anodes lose less metal than would be anticipated, and that the rolled anode is very inefficient.

Considered quantitatively, we have—

I. Rolled Anode.

The weight of nickel which should be deposited = $\frac{29.3}{31.8}$

$\times 0.568 = 0.525$ gram. Of this only $\frac{0.496}{0.525} = 0.945$, or 94.5 per cent. has appeared. We call this figure the **cathode efficiency**. The term will be explained in greater detail later.

Similarly 0.525 gram of nickel should have dissolved from the anode. Of this only $\frac{0.03}{0.525} = 0.057$ or 5.7 per cent. has dissolved. This percentage is called the **anode efficiency**.

II. Cast Anode.

(a) *Rough*.—Weight of nickel which should be dissolved and deposited = $\frac{29.3}{31.8} \times 0.92 = 0.847$ gram.

Hence, as above—

$$\text{Cathode efficiency} = \frac{0.771}{0.847} \times 100 = 91.2 \text{ per cent.}$$

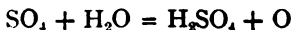
$$\text{Anode efficiency} = \frac{0.787}{0.847} \times 100 = 93 \text{ per cent.}$$

(b) *Smooth*.—Nickel equivalent to 0.614 gram Cu = $\frac{29.3}{31.8} \times 0.614 = 0.565$.

$$\text{Cathode efficiency} = \frac{0.529}{0.565} \times 100 = 93.5 \text{ per cent.}$$

$$\text{Anode efficiency} = \frac{0.305}{0.565} \times 100 = 53 \text{ per cent.}$$

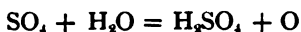
If nickel were being deposited and dissolved quantitatively, that is, in the quantity calculated by Faraday's laws, these efficiencies would be 100. Again, taking the case of the smooth cast anode, to say that the cathode efficiency is 93.5 per cent. means that 6.5 per cent. of the current did not deposit nickel, and in this case hydrogen gas appeared. An anode efficiency of 53 per cent. means that $(100 - 53) = 47$ per cent. of the current did not dissolve nickel as it should, but produced oxygen thus—



Further, in one vat an anode efficiency of 53 per cent. and a cathode efficiency of 93.5 per cent. together mean that $(93.5 - 53)$ per cent. of the current deposited metal without

dissolving it from the anode. As these are quite typical figures, small wonder that a nickel bath should become impoverished of its metal, and should need frequent additions of the salts. This is of great importance in the nickel bath and of considerable importance also in cyanide solutions where free cyanide is present in insufficient amount. In the acid copper bath, however, metal dissolves, and is deposited almost ideally, and hence little change of composition occurs even over extended periods of time.

Anode and Cathode Inefficiency.—Now, where the efficiency of the current is less than 100, the other part of the current has been producing other materials. Take the example of nickel already quoted. Here the anode efficiency is only 53 per cent., that is, 47 per cent. of the current has at the anode brought about the following reaction :—



producing sulphuric acid and oxygen. The amounts of these materials are also very definite. For 1 ampere-hour = 0.298 gram oxygen, and as 1 c.c. of the gas at N.T. and P. weighs 0.00144 gram, this amount represents—

$$\frac{0.298}{0.00144} = 207 \text{ c.c.}$$

With sulphuric acid, the chemical equivalent is 49, and the ampere-hour is therefore equivalent to—

$$0.001118 \times \frac{49}{108} \times 3600 = 1.83 \text{ gram}$$

Hence every ampere-hour of "inefficient current"¹ at the anode produces 1.83 grams of sulphuric acid and evolves 207 c.c. of oxygen.

Similarly at the cathode, if the efficiency is 93.5 per cent., then 6.5 per cent. of the current has done nothing more than

¹ "Inefficient current" means that which has not deposited metal at the cathode or dissolved metal from the anode.

deposit hydrogen. Now, 1 ampere-hour \equiv 0.0373 gram hydrogen. But 1 c.c. H = 0.00009 gram at N.T.P. And hence—

$$1 \text{ ampere-hour} = \frac{0.0373}{0.00009} = 414 \text{ c.c. H}$$

and for every ampere-hour which is inefficient at the cathode this volume of hydrogen is evolved. In the example under consideration the ampere-hour value is—

$$\frac{\text{copper deposited}}{\text{copper per ampere-hour}} = \frac{0.614}{1.182} = 0.52$$

At anode—

Efficiency was 53 per cent.

\therefore Inefficiency was 47 per cent.

Hence the amounts of sulphuric acid and oxygen formed were—

$$\text{Sulphuric acid} = \frac{47}{100} \times \frac{1.83}{1} \times 0.52 = 0.445 \text{ gram}$$

$$\text{Oxygen} = \frac{47}{100} \times \frac{207}{1} \times 0.52 = 50.5 \text{ c.c.}$$

At cathode—

Efficiency was 93.5 per cent.

\therefore Inefficiency was 6.5 per cent.

Hence the amount of hydrogen evolved was—

$$\frac{6.5}{100} \times 414 \times 0.52 = 14 \text{ c.c.}$$

Further, in this particular example the cathode efficiency was much in excess of the anode efficiency. The excess cathode efficiency over anode efficiency was—

$$93.5 - 53 = 38.5 \text{ per cent.}$$

Now, 1 ampere-hour \equiv 1.085 grams nickel. For each ampere-hour of the experiment, therefore, 0.385 ampere-hour

deposited nickel without dissolving any from the anode, this amount being—

$$\frac{38.5}{100} \times 1.085 = 0.417 \text{ gram}$$

Hence during the experiment the solution lost metal at the rate of 0.417 gram for each ampere-hour, an amount which is very considerable when reckoned over a few days, weeks, or months of working. It need hardly be necessary to further emphasize the importance of ensuring perfect anode solution if uniformity of working is to be maintained.

Weighing Metal during Deposition.—This, though by no means usual, may be done by suspending the work on the arm of a balance suitably disposed over the bath. The current is led from the bath through the balance. As deposition proceeds, the weight of the metal deposited is at once shown by adding weights to the other side of the balance. It must be observed, however, that such weights added do not represent the actual weight of metal deposited. As shown in Chapter XI. (p. 154), a solid weighed in a liquid apparently loses weight equal to the weight of liquid displaced. Thus 1 c.c. of copper weighs 8.9 grams in air. In water, however, it weighs less, the loss being the weight of 1 c.c. of water. Thus 1 c.c. copper weighed in water = 7.9 grams. If weighed in a liquid heavier than water the loss is greater and is equal to the weight of 1 c.c. of the liquid or its specific gravity. 1 c.c. copper in any liquid, therefore, weighs (8.9—sp. gr. of liquid) grams. Taking the sp. gr. of the acid bath as 1.18, then, in it—

$$1 \text{ c.c. copper weighs } 8.9 - 1.18 = 7.72 \text{ grams}$$

Thus every 7.72 grams of copper weighed in the solution represent 8.9 grams when weighed in air, and hence—

$$\text{Actual weight of copper} = \text{apparent weight} \times \frac{8.9}{7.72}$$

This expression can now be made of more general application, and thus with any metal or solution —

$$\left. \begin{array}{l} \text{Actual wt.} \\ \text{of metal} \end{array} \right\} = \left\{ \begin{array}{l} \text{apparent wt.} \\ \text{of metal} \end{array} \right\} \times \frac{\text{sp. gr. of metal}}{\text{sp. gr. metal} - \text{sp. gr. of liquid}}$$

Examples.

(1) Calculate the copper deposited by 20 amperes in $5\frac{1}{2}$ hours. (Ans. 130 grams.)

(2) What current will be required to deposit 1 lb. of copper in ten hours from the acid bath? (Ans. 38.4 amps.)

(3) How long will it take to completely corrode a copper anode weighing 1 cwt. in a copper sulphate solution with a current of 100 amperes? (Ans. 430 hours.)

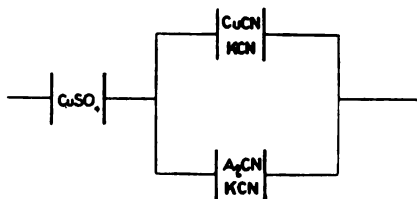


FIG. 89.

(4) A current of 5 amperes is passed through a mixed gas voltameter for fifteen minutes. What volume of gas will be evolved? (Ans. 776 c.c.)

(5) A sulphate of copper and a nickel bath are placed in series and a current passed. If for every 20 grams of copper there are deposited 15 grams of nickel, what is the current efficiency in the nickel bath? (Ans. 81.6 per cent.)

(6) A current is passed through copper sulphate and copper cyanide baths in series. At the end of an hour the following weights of copper have been deposited: 8.8 grams in the sulphate, and 14.3 grams in the cyanide bath. Calculate (a) the current, and (b) the cathode efficiency in the cyanide bath. (Ans. 7.44 amps. and 81.3 per cent.)

(7) Three baths are arranged as shown in Fig. 89, and a

current passed. At the end of a given time there have appeared 10 grams copper from the sulphate, and 12 grams copper from the cyanide solution. Assuming full efficiency in each case, how much silver will have been deposited?

NOTE.—To do this, first calculate the weight of copper (acid) equivalent to 12 grams of “cyanide” copper. Call the amount a grams. Then $10 - a$ grams copper acid have been deposited by the current passing through the silver bath. Calculate equivalent weight of silver. (Ans. 13.6 grams.)

CHAPTER IX

Processes Preparatory to Plating

Introduction.—The merest acquaintance with electro-deposition shows that success is largely dependent upon the state of the metal put into the bath. A greasy piece of work straight from the polishing mop can hardly be expected to retain a coating of nickel, nor could a bright deposit of that metal be reasonably expected on a rusty bicycle handle-bar. The greatest care is necessary in the preparation of work previous to insertion in the plating bath. The methods of preliminary treatment are both numerous and varied. They may be summarized under three heads :—

Mechanical Methods, comprising polishing, scouring, scratch-brushing, etc.

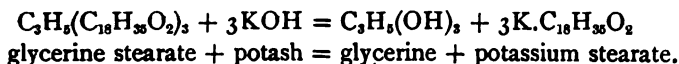
Chemical Methods for the removal of oxides or tarnish by dipping in acids or other solvents.

Electrolytic Methods, either for cleaning, for stripping a previous deposit, or for coating the work with a suitable deposit previous to the final plating.

The methods of treatment required by metals vary very considerably, and are indicated under the separate chapters on deposition. They cannot be very systematically arranged, and at this point only brief reference to some of these important operations can be made. It will be convenient to deal first with work which does not require any special preliminary stripping or polishing.

Removal of Grease by Potash.—Most metal work on leaving the hands of the manufacturer is covered with a layer

of grease. This is seen by the fact that water does not flow freely over its surface. A surface which uniformly retains the water is free from grease. Polishing materials are in most cases worked up with fatty materials, and grease remains after the polishing process. The merest film of grease may easily cause stripping, and work for plating should be entirely free from such material. It does not dissolve in water, and therefore washing with hot or cold water is quite inadequate for its removal. It can be best removed by converting it into soluble compounds. This is effected by scouring with hot potash. A chemical action occurs, and insoluble fat or oil is converted into other soluble compounds. Thus the usual fats and oils are compounds of glycerine and insoluble acids, of which stearic acid is an example. Its formula is $C_{18}H_{36}O_2$. Stearin is glycerine stearate. Then—



The potassium stearate is in reality soft soap, and produces a lather on the surface of the potash. Cold potash is not effective. It should be hot and moderately strong. Usually 1 lb. of American potash (a crude and less expensive form of potash) per gallon serves the purpose. A strong washing-soda solution serves the same purpose, but is slower in its action. This potash treatment should in every case be continued until—after thorough rinsing—water flows uniformly over the surface of the metal.

Potash, however, is not suitable for removing all kinds of oil. The ordinary burning oil (paraffin) or lubricating oil is not removed by potash. These are of different chemical composition, and require different treatment. When they are present the work should be first cleaned with mineral naphtha—a very light paraffin—and after removing the oil with a duster or cotton waste, the work may be scrubbed with slaked lime and finally passed through the potash. The work should only be passed for plating, when it is entirely free from grease. Different classes

of work must also be handled differently. Thus iron, copper, brass, etc., are quite unaffected by potash. On the other hand, articles of zinc, tin, Britannia metal, and pewter should be treated rapidly, as they are attacked by the potash, and dissolved.

The potash tank—preferably of wrought iron—may be heated by coke stove, coal fire, gas, or even waste steam passing through a coil contained in the tank. Small articles are treated in earthenware baskets or ladles, while larger articles should be suspended for a time in the bath before being scoured. Scouring is effected with a “potash mop”—a brush made with cotton instead of the ordinary bristle, as bristle is rapidly destroyed by hot potash (Fig. 90, *a*). There will also be removed with the grease an amount of dirt which is usually fixed to the metal by the grease.

Pickling and Dipping.—The grease being removed, the tarnish, rust, or oxide which is upon the surface of the metal, may now be attacked. Again materials must be selected which are suited to the purpose. Metallic oxides dissolve in acids. Such acid solutions are called **pickles** or **dips**. The term **pickle** is applied to weaker acids in which the metal is immersed for an appreciable time, while **dips** are stronger acids in which the immersion is only momentary. The function of each is to dissolve and thus remove the oxide. At the same time, however, they also remove the surface layer of the metal and thus loosen dirt and oxide which would not be dissolved. These pickles and dips are contained in acid-proof stoneware vessels, preferably fitted with loose covers. The nature of the acid used depends upon the metal to be cleaned, and will be treated under these headings:—

Iron and Steel.—The acid most commonly used is oil of vitriol, and only occasionally spirits of salts. The oxide attached to iron and steel is usually firm, and such work is treated in a pickle composed of—

Oil of vitriol	$\frac{1}{2}$ lb.
Water	1 gallon

From 15-20 or 30 minutes may be required to loosen the oxide sufficiently to enable it to be removed by scouring with a stiff brush and sand. A better effect may be produced when necessary by using a stronger acid, say—

Oil of vitriol	1 lb.
Water	1 gallon

and allowing only a shorter immersion ; but more usually the metal would be treated in the pickle first, and scoured, and subsequently passed through the stronger dip. Iron and steel with a very firm coating of rust or oxide would need polishing with emery, as described later.

Copper, Brass, German Silver, and similar metals and alloys, are most usually treated in nitric acid. These metals, after heat treatment, such as brazing or annealing, may be covered with an adherent black film consisting chiefly of copper oxide. Copper oxide dissolves most readily in nitric acid, and this acid therefore enters into the composition of pickles and dips for these metals. A suitable pickle may be made (1) by diluting down old dipping acid, which now contains a certain amount of metal in solution, with two or three times its volume of water ; or (2) by diluting fresh aqua-fortis with five or six times its volume of water. The work is left in this pickle from half an hour to one hour, according to the thickness and firmness of the scale. The work is removed, well rinsed in water, and scoured. The surface after pickling is usually dull, and can be considerably brightened by dipping.

Dipping acid consists chiefly of aqua-fortis with varying quantities of sulphuric acid. When passed through such a dip the surface of the metal acquires a clean appearance, and is then rapidly passed through two or more lots of clean cold water, then through hot water, and quickly dried in hot sawdust, either boxwood, beech, or mahogany. If the work is to be plated, it is passed directly to the solution after dipping and rinsing, or, for a more finished surface, it may first be scratch-brushed.

Zinc is usually cleaned first in potash. The immersion must

not be lengthy, owing to the fact that zinc dissolves quickly in the alkali. After rinsing it is passed through—

Oil of vitriol 1 lb.
Water 1 gallon

and subsequently scoured either with white sand or pumice powder.

Lead Alloys cannot be effectively treated in acids. Potash readily removes the grease, and after scouring with pumice powder or sand, to which lime has been added, the work should be ready for the plating bath.

Dead Dip.—A decidedly dead or frosted appearance may be imparted to brass work by dipping through acid of the following composition :—

Aqua-fortis 2 lbs.
Oil of vitriol 1 lb.
Zinc sulphate 50 grains

to which frequent small additions of common salt are made. The work is immersed for from three to five minutes, and is subsequently rinsed. If the surface is dull, the work is passed through the ordinary dip again, and thus becomes bright.

Bright Dip.—If the dipping acid contains more oil of vitriol (2 oil of vitriol to 1 of aqua-fortis—by volume), then a momentary dip prevents much corrosion of the brass or copper, and a brighter lustre is obtained.

Both these formulæ are capable of considerable modifications, according to the experience of those practised in the art.

A Cyanide Dip, containing $\frac{1}{2}$ –1 lb. of cyanide to a gallon of water, is most useful for purposes of removing tarnish from polished work. The tarnish is removed without any corrosion of the metal, leaving the polished surface in good condition. Most stains on silver or electro-plated goods are readily removed by this method, and the dip is also used as a last resort in preparing work for the nickel bath. The use of cyanide is



FIG. 90.—(a) Potash mops; (b) scouring brushes; (c) ordinary scratch brushes; (d) cup brush; (e) bottom brushes; (f) frosting brushes; (g) hand scratch knots.

(From Simmons' "Outlines of Electrical Engineering," by permission of Messrs. Cassell and Co., Ltd.)

based on the fact of the solubility of many metallic oxides in it.

Scouring mechanically removes dirt and oxide loosened in potashing and dipping. For this purpose bristle brushes of varying degrees of hardness are required (Fig. 90, *b*), and a number of materials are available.

Pumice, which is a porous product of volcanic eruptions, may be used in the form of lumps, or preferably in powders of different degrees of fineness. Pumice gives the surface a dull scratched appearance, and ordinarily the finest powder only should be used. To reduce the cutting effect it may be mixed with rotten stone, whiting, or even slaked lime. The surface produced by scouring with fine pumice is more conducive to adherent deposition.

Scratch-brushing is a form of wet polishing. It is performed with revolving brushes made with wires, either of steel, German silver, or brass of varying degrees of hardness. Fig. 90 shows a number of types of scratch-brushes (*c*) being used for ordinary work, (*d*) a cup brush for the inside of cups, etc., (*f*) frosting-brush, etc. These are attached to the spindle of a foot or power-driven lathe, provided with a tapered end, so that the scratch-brushing process tightens the brush. In order to render them more effective, a liquid is allowed to flow through a tube which leads on to the brush, or preferably just in front of it. Liquids used for this purpose are stale beer, weak washing-soda solution, diluted vinegar, or vinegar mixed with a little glue, or even soapy water. These considerably facilitate the process and assist in producing a finer surface. The work is pressed lightly against the revolving brush, which loses much of its value if the wires become bent. For ordinary purposes the wires used are of brass, German silver, or steel. For gold and silver and other soft metals, a fine soft brass brush is used, and as the metal under treatment increases in hardness, so the hardness and stiffness of the wire brush may be increased.

Scratch-brushing is required (*x*) either as an addition to, or in place of, scouring after dipping or pickling, when it frees

the surface of the metal from the loosened scale and imparts a measure of polish ; and (2) during or succeeding the plating process. Where thick deposits are being produced, occasional scratch-brushing tends to keep the deposit smoother, in rubbing down the tiny irregularities which invariably occur and develop on a plated surface. After deposition of a metal of a dull character, scratch-brushing provides the first stage in polishing. It must be remembered, however, that scratch-brushing rubs metal off rather than presses it down, and must not be applied too vigorously on a plated surface. It moreover cannot be applied on some classes of work, where the metal is hard, like iron and steel, or where the deposit has great hardness, like nickel or iron. An attempt to scratch-brush iron with a brass brush rubs metal from the brush on to the iron. Steel brushes are occasionally used in cleaning iron work.

Burnishing is applied to some deposits with a view to producing a polish without rubbing off the metal. Burnishers are smooth tools of hard steel or agate. They are of different shapes, as shown in Fig. 91, for different types of work. When rubbed across a silver deposit, for example, and lubricated by a liquid similar to that used for scratch-brushing, they produce a bright mark, and the rubbing is continued until the surface is smooth and uniform. After rinsing and drying, a minimum of polishing serves to give the work the final lustre. The tools require continued polishing, and this is done by rubbing them frequently along a leather strap fastened to the bench, to which putty powder is applied. Agate burnishers are by far the more expensive, and produce a better result. They are therefore used for finishing. It will be observed that burnishing rubs the metal down, producing a more compact and harder metal, in addition to imparting to it a dull lustre.

Polishing has the twofold object of smoothing and imparting lustre. Microscopically, any smooth surface consists of an enormous number of very fine scratches, and polishing consists of replacing irregularities on the surface of a metal by a regular

series of scratches, at first somewhat pronounced. These scratches are then substituted by series of finer scratches, the

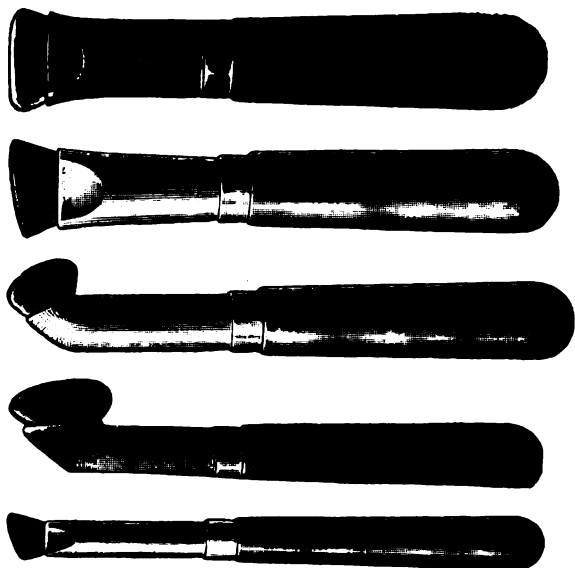


FIG. 91A.—Agate burnishers.



FIG. 91B.—Steel burnishers.

finest of all constituting the polished surface. In polishing, therefore, there are three chief points—(1) the material to be

applied ; (2) the medium for its application ; and (3) the method of application. It is performed largely on power-driven lathes, apart from which the work would be very laborious. The scratching or abrasive material is usually applied on *bobs* and *mops*. Bobs (Fig. 92) are circular discs made of wood, leather, or felt of various thickness, the diameters varying from 2 inches to 36 inches. In order to minimize material, wood can be used, and the edge covered with leather or felt. They are revolved at a speed of 500-2000 or more per minute, and the polishing substances applied either by merely

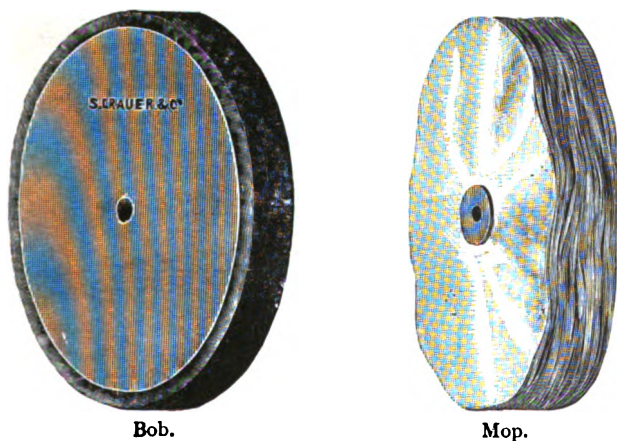


FIG. 92.

rubbing or by glueing. The work to be polished is then pressed against the revolving bob, and moved about until a uniform and satisfactory result is obtained. Mops consist of a series of discs of linen, calico, or swansdown firmly secured at the centre, and stitched or riveted at intervals. While loose when at rest, they become very stiff when revolving at the usual speed of 1000-2000 revolutions per minute. Two small leather discs on either side serve to bind them together, and provide also a more durable material for fastening on to the lathe spindle. The diameter

of the mops varies from a few inches up to 18 inches or more, and up to $1\frac{1}{2}$ inches in thickness. The polishing materials are applied either in the form of powder, paste, or a solid composition, frequent application being made during the polishing process. Mops are used for the finer grades of polishing. In addition to the ordinary flat bobs and mops, smaller sizes and special shapes are made to meet the requirements of different classes of work. These consist usually of wooden shapes covered with an appreciable thickness of felt or other material. Fig. 93 shows a polishing lathe with fast and loose pulleys.

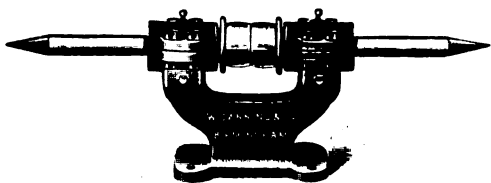


FIG. 93.—Polishing lathe.

It may be mounted on a firm wooden table or preferably on an iron stand. For small work a wooden tray is suitably mounted to hold the materials. For large work this is dispensed with.

Materials for Polishing.

Emery in the form of powder of different degrees of fineness is used for the rougher kind of work. Emery is an oxide of aluminium which in this natural form is very hard. It is applied to bobs of leather and felt by first turning these down to a level surface, treating them with glue and rolling them in the emery powder. When quite dry they are placed on the spindle and revolved, while a hard smooth surface is brought against them. This serves the purpose of detaching loose fragments of the emery and of pressing into the soft leather or felt that which has become attached by the glue. The bob is then ready for use. Emery can be obtained in

very many different grades, from a coarse powder down to what is called "flour" emery.

Sand.—Trent sand is most commonly used, mixed with a small quantity of oil to make it more adhesive. It is used for rough work with calico mops, and is fed by hand by the operator upon the work. By means of this material file marks and emery marks are readily removed from brass. The sand can be used repeatedly, and, losing some of its cutting power by wear is still used for the finer grade of work.

Tripoli is a siliceous earth with fine cutting properties. It is used chiefly in the form of compositions in which the tripoli of different degrees is mixed with a solid fat. The material is thus applied by pressing it to the revolving mop frequently during the polishing process.

Crocus and rouge are forms of oxide of iron. They are used for the finishing stages of the process, being applied either in the form of compositions, or mixed with water and used as a paste.

Sheffield Lime is used especially for the finishing stage of nickel polishing. It is obtained by calcining the limestone from the Sheffield district. It consists of dry lime, and should be quite free from grit. Owing to the ease with which it takes up moisture and carbonic acid gas from the air, and becomes converted again into chalk, it should be kept in tins with well-fitting lids. When a lump of the lime is pressed against a revolving mop the rough edges of the mop take off and retain sufficient lime for polishing, and this produces the finest finish upon nickel.

Electrolytic Cleaning.—Methods applying the electric current to the cleaning of work are now in considerable use, and the following summary ¹ of directions for this work will give an idea of the process. The work to be cleaned is made the anode in the ordinary hot potash bath, the iron tank being the cathode. A current is applied for a short time, and the grease is rapidly removed. In its place a brown stain appears on the

¹ *Trans. Faraday Soc.*, vol. ii., 1906, p. 53.

work, which can only be removed, by acid dips or cyanide, with difficulty. To effect the removal of the stain the current is reversed for a short time, the work becoming the cathode. It is claimed that by such a method work can be cleaned more thoroughly, more expeditiously, and with far less labour than by the ordinary scouring process. No explanation of the mechanism of the changes is ventured, but this is probably accounted for by the fact that nascent oxygen first given off at the anodic work effects the oxidation of the grease to soluble compounds and also produces the stain of metallic oxides, the stain being subsequently decomposed and removed by the nascent hydrogen produced at the work, when it becomes the cathode on reversing the current.

CHAPTER X

General Properties and Preparation of Solutions

IN selecting substances suitable for plating solutions, many points must receive attention. Depositing solutions must possess certain well-defined properties, and at the same time other properties of a detrimental character must be absent. Seldom can all the properties, which individually are desirable, be combined, and hence a choice must be made to obtain the most efficient combination. It is surprising that of so many metallic compounds, so few are available for the production of reguline deposits, though in many cases the desirable properties may be introduced through the medium of other substances.

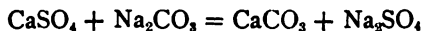
Simplicity of Composition and Ease of Preparation.—Solutions should, if possible, be of simple composition and capable of easy preparation. The more complex the solution, the greater will be the difficulty in tracing the source of any trouble which may arise. *No substance should be present without it serves some definite purpose.* Then it should be present in correct quantity, and an exact record of the amount should be kept. In case of doubt, too small rather than too large a quantity should be added. More can easily be added if required, but it may not be easy to take out an excess. If a trial experiment is made on a small bulk, a simple calculation will then serve to show the correct quantities for a larger bulk. Small quantities of impurities may produce startling changes. No better example of this can be quoted than that of the addition of a little carbon disulphide to the silver bath, when

the dull deposit of silver is changed so effectively to one which is bright. The bright plating bath contains only 1 oz. of carbon disulphide in 250 gallons of the solution, and a slight excess results in a dead deposit with a tendency to blackness. Seeing, then, that the effect of impurities is so pronounced, and that such impurities may find their way into the solutions accidentally, considerable care must be exercised. The solutions should in the first instance be made as pure as possible. In preparing them chemically, excesses should be avoided, and precipitates should be well washed with water. Pure materials should be used as far as possible. Some years ago cyanide was sold in large quantities containing only 30-40 per cent. of KCN. For every 3 lbs. of this substance used, 2 lbs. impurities serving no useful purpose whatever were introduced into the solution, making its composition more complex, and increasing the difficulty of readjusting it, in case of error.

Water.—Most waters supplied by the companies contain appreciable amounts of dissolved solids, such as calcium bicarbonate and calcium sulphate. These salts render water **hard**, that is, they impart a difficulty in producing a lather with soap. When the hardness is due to calcium bicarbonate (bicarbonate of lime) it can be considerably or completely reduced by boiling, carbonic acid gas being expelled and chalk precipitated—

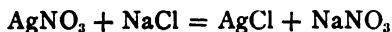


Such hardness, removable by boiling, is called **temporary hardness**. The hardness produced by calcium sulphate is not removed by boiling, and is therefore called **permanent hardness**. It may, however, be removed by the addition of sodium carbonate (Na_2CO_3)—



In addition to these compounds, however, other salts of

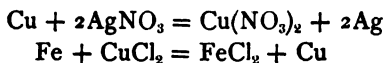
calcium, magnesium, sodium, and potassium are usually present. In such waters, clear solutions of silver nitrate, copper sulphate, nickel salts, etc., cannot be made. The silver nitrate is affected by soluble chlorides, silver chloride being formed and precipitated—



while soluble carbonates and bicarbonates produce turbidities and precipitates with many metallic salts. To prepare a clear solution of a silver salt, distilled water or filtered rain-water must be used, preferably the former, while the effect of the carbonates in water can usually be counteracted by the addition of a small quantity of the acid corresponding to the salt, and in some solutions, such acid is advantageous in adding conductance¹ to the solution.

Stability of Solutions.

(1) **Against Metal to be Plated.**—It is well known that many metallic solutions readily give up their metal in contact with a more positive metal. Thus—



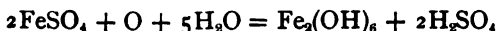
As the negative metal is deposited, so the positive metal passes into the solution in equivalent quantity. Hence the more negative metal is being deposited by what is called “simple immersion,” upon a foundation of metal which is being dissolved away. It is therefore most unlikely that such deposits will be adherent. Under the most favourable conditions the deposit may withstand the rubbing action of the fingers, but cannot, as a rule, withstand the ordinary frictional processes of burnishing or polishing. If this simple immersion

¹ “Conductance” = the power of facilitating the passage of electricity through it.

occurs in a plating solution, whatever metal may be superimposed by electrolysis, the adhesion is poor, and stripping is most likely to occur during the subsequent finishing processes. Hence copper is not deposited upon iron from the sulphate solution, nor silver upon copper from the nitrate solution. (Note that in the silver voltameter mentioned in Chapter VII. silver nitrate is used, but only in contact with a much more negative metal, platinum.)

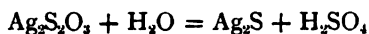
It becomes necessary, therefore, to choose more stable compounds, and from a solution of copper cyanide iron does not deposit copper by simple immersion, while in the case of silver cyanide the solution, while not entirely stable against all the metals which may be put into it, gives up its metal much more slowly, and to minimize the action of the metal upon the solution the current should be applied as soon as the metal is placed in the bath. The wide use of potassium cyanide in plating solutions is due to the greater stability of its compounds with the metals. As a general rule the deposition of a negative metal upon one more positive is conducted by cyanide solutions, while in the case of the deposition of such positive metals as iron and nickel, the ordinary salts are serviceable.

(2) **Against Air.**—A solution should, if possible, suffer no change on exposure to air. Copper and nickel sulphates are very stable. Ferrous sulphate, however, readily undergoes oxidation with the formation of a thin layer of ferric hydroxide, $\text{Fe}_2(\text{OH})_6$, thus—



and this prevents the formation of a clear solution even in distilled water, which may still contain sufficient oxygen to effect this change. Usually the ferric hydrate forms a thin layer on the top of the solution, and to some extent this prevents further oxidation. For making up such a solution, distilled or filtered rain-water should be well boiled before being used, to get rid of dissolved air.

Again, all solutions containing cyanides are unstable in air, and the feebly acid properties of carbonic acid gas bring about some decomposition. The presence of other acid fumes will also be injurious to such solutions, and vessels or vats containing cyanide solutions should not be unnecessarily exposed. In fact, so very unstable are the cyanides of potassium and sodium that they even decompose in water, and give rise to several products, most of which, however, are without injurious effect. Silver salts generally are unstable, and the double iodide (AgI.KI) and double thiosulphate ($\text{Ag}_2\text{S}_2\text{O}_3.\text{Na}_2\text{S}_2\text{O}_3$), which have at one time been suggested to replace the poisonous cyanide solutions, suffer decomposition, in the latter case black silver sulphide being deposited—



Conductance.—Electro-plating solutions should offer little resistance to the passage of the electric current. The greater the conductance the lower the P.D. required to maintain the necessary current density, and where current is being used on a large scale, the costs are proportionately low. Now, very few metallic salts used in plating are good conductors in solution. They do not compare at all with the common acids. Sulphuric acid (dilute) is a much better conductor than copper sulphate. There arises, therefore, the necessity of imparting conductance to the plating solution. A good example is that of the sulphuric acid in the acid copper bath. Such a substance should exert no marked action on either anode or cathode, and for this reason this acid cannot be added to the iron and nickel solutions. With iron it would dissolve the anode much too freely, besides hindering the deposition of the metal, and similar actions occur with the nickel bath. In these examples the sulphuric acid yields a cation (hydrogen) which is much more easily deposited than iron or nickel, while of copper and hydrogen the former is more easily deposited, thus preventing polarization in the

Daniell cell, though in the copper cyanide solution it can be freely deposited with the metal without any prejudicial effect.

Cyanide solutions most frequently contain an excess of potassium cyanide. While this adds somewhat to the conductance, this is not its chief function. For imparting conductance it does not compare with sulphuric acid. The chief purpose served by the free cyanide is that it keeps the anodes free from insoluble single cyanides which, if collected on the anode, add considerable resistance to the bath.

In nickel solutions the practice of adding common salt to the electrolyte is sometimes resorted to. In this case probably a large share of the current is due to the movement of the sodium and chlorine ions, and at the cathode the sodium ions displace the nickel which is deposited on the work.

Again, conductance in solutions is considerably increased by a rise of temperature. In this respect, electrolytic solutions behave in a manner different from solid conductors. Heating increases the resistance of solid conductors, but diminishes that of most liquid conductors, and a considerably lower E.M.F. is required with a warm solution than with one which is cold. Even the difference of temperature between the heat of summer and the cold of winter is sufficient to make an appreciable difference to the working of a bath. Warming the solution also facilitates the solution of anode deposits, and for many solutions is to be recommended, a temperature of 50–60° C. being sufficient.

Cleansing Properties of a Solution.—A most desirable property in a plating bath is the ability of the solution to remove the slight films of tarnish which may, with the utmost care, occur on work when ready for deposition. However careful the operator may have been, there is usually time between the final stage of cleaning and the immersion in the bath for some appreciable film of tarnish to form. These films of oxides and sulphides may often be sufficient to prevent the adhesion of the deposit, and the ease with which stripping will sometimes occur is marvellous. Such films, however,

might be removed by an agent in the solution which may be present for another purpose. Sulphuric acid and free cyanide provide good examples. The readiness and rapidity with which a film of electro-deposited copper will tarnish is well known, but the ease with which it is removed by a momentary re-immersion in the solution is not less surprising. If the work also contained a similar tarnish this would no doubt be similarly removed, by allowing the work to hang in the solution for a few moments before switching on the current. Cyanide of potassium possesses good cleansing properties, and most compounds of the ordinary metals are soluble in it. So effective is it that it is common practice to rinse work about to be nicked through a cyanide solution ($\frac{1}{2}$ lb. per gallon), again thoroughly rinsing in water just previous to immersing the work in the bath, as the nickel solution does not contain any compound which exhibits cleansing properties in the slightest degree, and this accounts very considerably for the trouble which is experienced in nickel-plating.

It must be clearly understood, however, that though some of the plating solutions possess these cleansing properties, no effort must be spared to ensure a thoroughly clean surface before the work enters the solution. The ordinary methods must be pursued with the utmost rigour, and the plating solution must not be depended upon even to remove last traces. After every effort has been made to secure scrupulous cleanliness, then in those solutions containing cleansing materials a momentary suspension without the current will be an advantage, but in solutions which do not contain cleansing materials, the current must be switched on immediately, and a deposit obtained as quickly as possible before oxidation can occur. This rapid deposition of the first coating is called "striking," and is referred to elsewhere.

Solutions should yield Reguline Deposits.—The number of metallic compounds available for electro-deposition is somewhat limited by this condition, that a deposit of a good coherent character must be produced. Stannous chloride, for

example, yields a deposit of beautiful long crystals of tin. The deposit from lead acetate is of the same character, though the crystalline form is not so well developed. Such compounds are therefore useless for the electro-deposition of these metals. In each case alkaline solutions are much more satisfactory, but an astonishing improvement can be effected by the addition of a small amount of glue or gelatine, the quantity not exceeding a few grams per gallon. By this simple addition, dark powdery deposits at once give place to whiter, more granular and perfectly coherent deposits, and occasional small additions of the glue or gelatine must be made. The reason for this great change is open to discussion, and the great change produced by these substances is somewhat akin to the production of the bright silver deposit. Failing some adequate explanation the fact may still be applied, as has been the case in the development of commercial methods of depositing these metals. The effect of glue or gelatine on the allowable C.D. in the acid copper bath is, however, much less marked.

General Methods of Preparation of Solutions.

All methods for the preparation of electro-depositing solutions may be grouped as follows:—

- (1) **Electrolytic Method.**
- (2) **Chemical Methods.**

Electrolytic Method.—This is a method which is perfectly applicable for all solutions, but while practicable in some cases, would be hopelessly impracticable on the large scale for others. It involves making the metal the anode in an acid or salt solution which will supply the anion required (Fig. 94). On using a carbon or metal cathode standing in a porous cell containing some of the electrolyte, and passing the current, the anode dissolves without deposition at the cathode. The amount of metal passing into the solution can be ascertained by weighing the anode from time to time. By this method a copper anode in sulphuric acid would form copper sulphate,

but it would obviously be cheaper and much more convenient to dissolve bluestone in water. For silver and gold solutions the method is frequently employed, the metals forming the anode in a cyanide solution. By withdrawing the porous cell and substituting a small piece of work, the condition of the solution can at once be determined, and the process continued until a satisfactory result is obtained.

Chemical Methods.—Some salts are easily and cheaply purchased, and need only to be dissolved in water. Copper

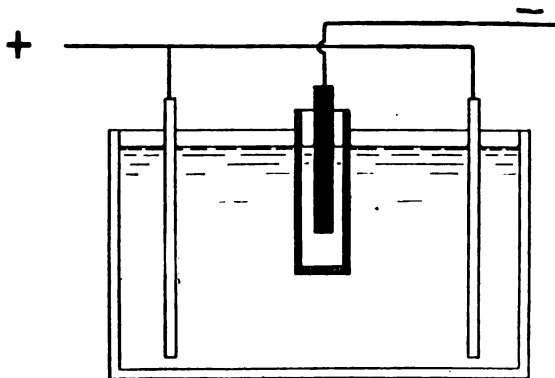


FIG. 94.—Electrolytic preparation of solution.

sulphate, nickel salts, and iron ammonium sulphate are examples. While the process of solution is only one of fine division, steps may be taken to facilitate the process. Crystals of nickel salts thrown to the bottom of a tank of water might remain there for years without properly dissolving. All crystals should be at least roughly crushed and suspended by perforated stoneware baskets or muslin bags in the water in which they are to be dissolved. As the solid dissolves the solution formed is heavier than water, and therefore sinks, giving rise to a gentle circulation which constantly brings the weaker solution into contact with the undissolved solid. Again, as a general rule, solids are more soluble at an

elevated temperature, and warm water will dissolve a much larger proportion of the salt, and it may often be convenient to dissolve most of the salts in a smaller bulk of warm water, and add this strong solution to more cold water contained in the tank.

In cases where the sufficiently pure substance cannot readily be procured, the more common salts, or even the metals themselves, provide a starting point, and from these the required substances can be made, preferably through an intermediate insoluble compound from which the impurities can be washed. The details will be found in subsequent chapters dealing with the metals and solutions.

CHAPTER XI

Density of Solutions—Hydrometers

Definition.—As a rule, when a solid substance is dissolved in water, the solution produced is heavier than the water when equal volumes or bulks are compared. This is usually expressed in the form “that the specific gravity or density is increased.” By **specific gravity** or **density** we mean the *relative* weight of a solid or liquid as compared with the weight of an equal volume of water. Thus a pint of water weighs $1\frac{1}{4}$ lbs. (av.), or 20 ozs., while a pint of mercury weighs 272 ozs. The mercury is obviously much heavier than the water. It is exactly $\frac{272}{20} = 13.6$ times as heavy; 13.6 is the specific gravity or density of mercury. Similarly, a pint of sulphuric acid weighs 36.8 ozs., and the specific gravity of the acid is therefore $\frac{36.8}{20} = 1.84$. The trouble of even a simple division may be avoided by taking a measure and marking on it the level attained by exactly 1 lb. of water. With any other liquid standing in the measure at this level its weight in pounds at once represents its specific gravity. In determining specific gravity, however, it is unusual to deal with large quantities. Smaller quantities, say, 25 c.c., are sufficient. This quantity may be drawn out from the bulk of liquid by a pipette, or measured off from a burette. The liquid can then be delivered into, and weighed in, a flask.

Example.

Weight of flask = 25.36 grams

Weight of flask and 25 c.c. water = 50.26 „

Weight of 25 c.c. water = 24.90 „

At ordinary temperature, say, 15°C ., 25 c.c. of water weigh less than 25 grams, for it is only at 4°C . that 1 c.c. water weighs 1 gram. At a higher temperature the water expands, that is, the same mass of water occupies a larger volume, or the same volume contains less water. It is therefore lighter. Further—

Weight of flask and 25 c.c. sulphuric acid = 71.18 grams.

Weight of flask = 25.36 „

45.82 „

Hence—

$$\begin{aligned}\text{Specific gravity of the acid} &= \frac{\text{weight of 25 c.c. of acid}}{\text{weight of 25 c.c. of water}} \\ &= \frac{45.82}{24.90} = 1.84\end{aligned}$$

As, however, the specific gravity of water varies only very slightly with slight differences of temperature, it serves for many practical purposes to consider 1 c.c. as weighing 1 gram, and hence the weight of 1 c.c. of any solid or liquid *expressed in grams* is at once the specific gravity.

Determination of Specific Gravity.

(1) **Solids.**—One method in most common use may be described. It is based on the fact discovered by Archimedes in 220 B.C. that when a solid is immersed in water, the solid appears to be lighter, and the apparent change in weight is equal to the weight of the water displaced. Now, the volume of water displaced is obviously the volume of the solid which displaces it, and therefore as 1 gram of water is equal to 1 c.c., the loss of weight of the solid in grams represents the weight (in grams) of water displaced, and also its volume (in c.c.), and therefore the volume of the solid in c.c.

Example.

Weight of solid in air = 45.50 grams

Weight of solid in water = 40.38 „

Loss of weight = 5.12 „

\therefore Weight of water displaced = 5.12 grams

\therefore Volume of water displaced = 5.12 c.c.

\therefore Volume of solid = 5.12 ,,

Hence, if 5.12 c.c. solid weigh 45.50 grams, 1 c.c. weighs $\frac{45.5}{5.12}$ grams, and specific gravity = 8.9.

Method.—For the purpose of this experiment, the solid is suspended from the hook of the balance by a fine thread, and weighed. It is then surrounded by water contained in a suitable vessel supported on a bridge, as shown in Fig. 95,

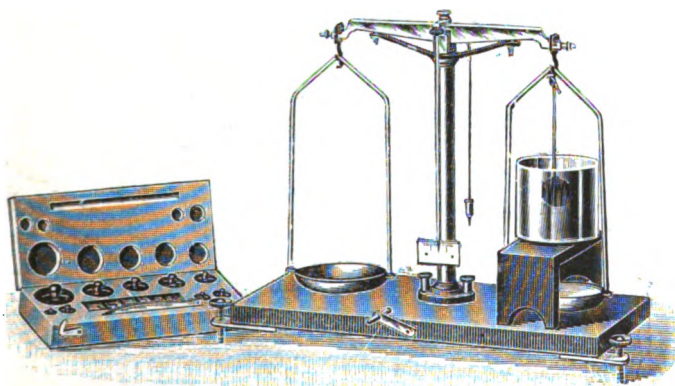


FIG. 95.—Determination of specific gravity of a solid.

allowing the balance to swing freely. The water should be sufficient to completely cover the solid while it is weighed. The method has to be modified for light solids, which usually float on water, and for those which are soluble in water.

(2) **Liquids.**—The specific gravity of liquids may be readily determined by a number of methods. Two factors are required, viz. the weight and volume of a given quantity. The weight may be easily and accurately determined by means of a balance. It is the measurement of the volume, however, which supplies the usual difficulty. This can be accomplished by the use of a **specific gravity bottle**. This is shown in

Fig. 96, being a small bottle with a well-fitting ground glass stopper, through which there is a fine hole. In using the bottle it is first cleaned and dried, and its weight obtained. The stopper is removed and it is filled with distilled water. The stopper is then inserted, and excess of liquid is expelled through the hole in the stopper. It is then thoroughly dried on the outside, and reweighed. The increase of weight gives the weight of water (grams) and the volume in cubic centimetres. The water is then run out and the



FIG. 96.—Specific gravity bottle.

be tested, and finally filled with this liquid, inserting the stopper as before. After drying again and weighing we have the weight of this volume of the liquid, from which—

$$\begin{aligned}\text{Specific gravity of liquid} &= \frac{\text{weight of liquid (grams)}}{\text{volume of liquid (c.c.)}} \\ &= \frac{\text{wt. of liquid (gms.)}}{\text{wt. of same volume of water (gms.)}}\end{aligned}$$

Example.

Weight of sp. gr. bottle and distilled water = 44·172 grams.

Weight of bottle alone = 19·200 „

Weight of water = 24·972 „

Weight of bottle and liquid = 46·845 „

Weight of bottle = 19·200 „

Weight of liquid = 27·645 „

$$\text{Hence sp. gr. of liquid} = \frac{27·645}{24·972} = 1·107$$

This provides the most accurate method available for ordinary work. It will be observed that the above method can only be strictly accurate when both liquids are at the same

temperature. This condition may soon be attained if both liquids have been allowed to stand in the air for a short time.

The capacity of a specific gravity bottle is usually marked on it, and a definite temperature, say, 15°C. , is also shown. So long as both liquids are at the same temperature this volume may be disregarded, as it is unnecessary when we weigh the water.

Such a specific gravity bottle can be bought for one shilling or even less.

Use of Pipette.—If such a bottle is not readily procurable, the approximately equal volumes may be obtained by measuring out 10, 15, 20, or 25 c.c. by means of a pipette, and weighing these volumes contained in a small flask. This method is quite accurate enough for all ordinary work.

Example.

Weight of flask and 25 c.c. distilled water = 41.195 grams

Weight of flask alone = 16.256 „

Weight of water = 24.939 „

Weight of flask and 25 c.c. liquid = 43.832 „

Weight of flask alone = 16.256 „

Weight of liquid = 27.576 „

$$\text{Hence sp. gr. of liquid} = \frac{27.576}{24.939} = 1.105$$

For this experiment the flask need only be dried on the outside, but after throwing away the water it should be reweighed before adding the liquid. Further, to save time, the 25 c.c. of liquid may be directly added to the water in the flask, and the result obtained as follows :—

Wt. of flask = 16.256 } \therefore Wt. of water

Wt. of flask and water = 41.195 } = 24.939

Wt. of flask, water, and liquid = 68.771 } \therefore Wt. of liquid = 27.576

Hydrometers.—For many workshop purposes it is required to know the specific gravity of a solution or liquid with only approximate accuracy so long as it is quickly determined.

Instruments made for this purpose are called **hydrometers**. They are usually made of glass, though for some purposes metal hydrometers may be and are used. They consist of weighted bulbs to which is attached a stem carrying a graduated scale. They are made of such size and shape that they will float in a vertical position in the liquid. Then the heavier the liquid, the further will the hydrometer be forced out. They may then be divided into two classes :—

(1) **Constant Immersion Hydrometers**.—On such hydrometers there is a mark on the stem, and on a pan at the top of the hydrometer weights are added in order to sink the hydrometer till the mark coincides with the level of the liquid. The heavier the liquid, the greater is the weight required to sink the hydrometer down to the mark. This form, however, is not used in the workshop.

(2) **Variable Immersion Hydrometers**.—In this kind the stem carries a graduated scale usually reading downwards,



FIG. 97.—
Common
form of
hydrometer.

so that in a heavier liquid the hydrometer is partially forced out, and a higher reading coincides with the level of the liquid. A common form of hydrometer is shown in Fig. 97. The real difference, however, between the various hydrometers of this class, is not their shape or size, but the manner in which the scale is graduated. Thus with any of the forms, imagine that there was no graduated scale provided. The instrument would not necessarily be useless. We might construct our own scale upon it by taking a number of liquids, and determining their specific gravity by using the specific gravity bottle. The hydrometer could then be placed in these liquids successively, and a mark scratched upon the stem at the points where the levels of the liquids touch. From these points

representing definite specific gravities, a simple scale could be constructed, and the instrument would then become available for ordinary use.

Now if a number of similar instruments were made, similar printed scales could be inserted in the stem before this was finally sealed. This is practically what is done in the ordinary hydrometers. Common types of hydrometers are—

(1) **The Direct Reading Instrument**, on the graduated scale of which the specific gravity is read as the mark coincident with the level of the liquid. This would at once appear the most easy method, and indeed such hydrometers are in common use.

(2) **The Beaumé Hydrometer**, the scale readings of which do not directly mean specific gravities. When this instrument is in use the number is observed which most nearly coincides with the level of the liquid. Then the actual specific gravity is obtained by reference to the following table, which may accompany the hydrometer.

TABLE X.

COMPARISON OF SPECIFIC GRAVITY AND BEAUMÉ READINGS.

Degrees. Beaumé.	Specific gravity.	Degrees. Beaumé.	Specific gravity.
3	1.02	39	1.361
6	1.041	42	1.401
9	1.064	45	1.442
12	1.088	48	1.485
15	1.113	51	1.531
18	1.138	54	1.578
21	1.166	57	1.634
24	1.195	60	1.690
27	1.225	63	1.750
30	1.256	66	1.815
33	1.289	69	1.885
36	1.324	72	1.960

If, then, the level of the liquid should be between two numbers an intermediate value of the specific gravity will be taken. Thus a reading on the hydrometer of 21 would correspond to a specific gravity of 1.166, while a scale reading of 28 may be

taken to represent a specific gravity of 1·235 (*i.e.* one-third between 1·225 and 1·256). In the absence of such a table the specific gravity may be approximately obtained from the following expression¹:—

Specific gravity = $\frac{147}{147 - x}$, where x is the reading on the scale. Thus:—

(1) Reading on scale = 18

$$\text{Specific gravity} = \frac{147}{147 - 18} = \frac{147}{129} = 1\cdot139$$

(2) Reading on scale = 60

$$\text{Specific gravity} = \frac{147}{147 - 60} = \frac{147}{87} = 1\cdot689$$

This hydrometer is widely used.

(3) **The Twaddell Hydrometer.**—This, again, differs from the Beaumé only in the graduations on its stem. Its scale readings are merely degrees from which the specific gravity may be obtained by reference to Table XI.

TABLE XI.

COMPARISON OF TWADDELL READINGS AND SPECIFIC GRAVITY.

Degrees Twaddell.	Specific gravity.	Degrees Twaddell.	Specific gravity.	Degrees Twaddell.	Specific gravity.
0	1·000	50	1·250	100	1·500
5	1·025	55	1·275	105	1·525
10	1·050	60	1·300	110	1·550
15	1·075	65	1·325	115	1·575
20	1·100	70	1·350	120	1·600
25	1·125	75	1·375	125	1·625
30	1·150	80	1·400	130	1·650
35	1·175	85	1·425	135	1·675
40	1·200	90	1·450	140	1·700
45	1·225	95	1·475	144	1·720

¹ The expression specific gravity = $\frac{144}{144 - x}$ is usually given. It will be found, however, that the one given above, viz. $\frac{147}{147 - x}$, gives results more nearly in accordance with the table.

It will be observed that these figures run in a very orderly manner—in fact, the decimal part of the specific gravity is just five times the scale reading. A simple expression can therefore be used to quickly calculate the specific gravity from the reading on the hydrometer; thus—

$$\text{Specific gravity} = \frac{(n \times 5) + 1000}{1000}, \text{ where } n = \text{scale reading.}$$

Example.

Scale reading = 47

$$\therefore \text{Specific gravity} = \frac{(47 \times 5) + 1000}{1000} = \frac{1235}{1000} = 1.235$$

The Twaddell hydrometer has a wide range—from 1.000 to 1.720. In order that all these readings shall not be crowded upon one inconveniently long scale, the instruments are made in sets of six of increasing weight. The range of each instrument is roughly as follows :—

No. 1.	Scale reading	0- 24	Sp. gr. 1.000-1.120
„ 2.	„	24- 48	„ 1.120-1.240
„ 3.	„	48- 72	„ 1.240-1.360
„ 4.	„	72- 96	„ 1.360-1.480
„ 5.	„	96-120	„ 1.480-1.600
„ 6.	„	120-144	„ 1.600-1.720

In using the instruments the lightest (No. 1) is tried first. If the stem is entirely forced out by the heavy solution, No. 2 is next tried, and so on, until a scale reading is obtained. In every case a hydrometer should be rinsed and dried before passing from one solution into another.

Comparison of Beaumé and Twaddell Scales.—

As both of these instruments are in common use, a comparison of their readings is desirable. This can be best done graphically in the following manner. Starting with a piece of squared paper (Fig. 98), select two lines, OA and OB, at right angles. The line OB is now divided into a scale of specific gravity from 1 at the point O to 1.72 at the point B. On OA

M

mark a scale of degrees from 0 at the point O to 144. Dealing with the Twaddell readings, first select a number of scale readings from the table on p. 160, and lightly mark them on the vertical scale. From these points draw a number of very faint horizontal lines. Next take the specific gravities corresponding to these readings; and mark them on the horizontal scale. From these points draw very faint vertical lines until these intersect the corresponding horizontal lines. A

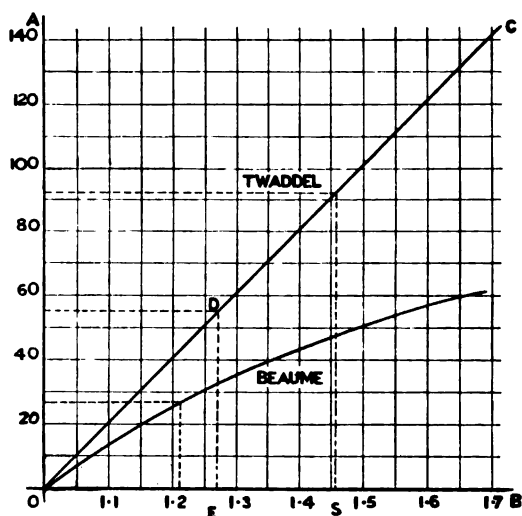


FIG. 98.—Comparison of Beaumé and Twaddell scales.

number of points are thus produced, and an attempt at joining them will produce a straight line, which passes through the point O. By means of such a line any scale reading is at once converted into its specific gravity, and *vice versa*. Thus, taking a scale reading of 55, run a faint horizontal line until it cuts the line OC at D. From this point drop a vertical on to the line OB (the scale of specific gravity). It cuts this scale at a point E, which corresponds to a specific gravity of 1.275. Similarly prepare a number of points from the

Beaumé table on p. 159. The points thus formed do not produce a straight line when joined. The line, however, is a uniform curve, which begins at the point O. This curve may be used in the same way as the straight line for the Twaddell readings. Thus 27 degrees Beaumé is found by drawing a horizontal line till it cuts the curved Beaumé line, and dropping a perpendicular to the specific gravity scale to correspond to a specific gravity of 1.225. In a similar manner degrees Beaumé may be converted into degrees Twaddell, and *vice versa*. Thus at any point, S, draw a vertical line until it cuts both curves. These points of intersection give equivalent readings on the two scales, and hence $47^{\circ} \text{ B.} = 93^{\circ} \text{ Tw.}$

Other Instruments.—Besides these standard instruments there is a large variety of others usually designed for special purposes. Fig. 99 shows a particular form which may be conveniently used to show the specific gravity of accumulator acid. It is hung on the inside of the accumulator cell. Its hollow stem, into which the liquid has access, contains a number of glass beads weighted to correspond to different specific gravities. If the instrument is placed in water, then all these balls being heavier than water sink. In a heavier liquid some balls rise. If we place the hydrometer in water, and sulphuric acid is added (and this is really what happens in charging an accumulator), then with increasing specific gravity the balls rise one by one, and the specific gravity of the liquid can be approximately determined. Thus the beads may correspond to specific gravities of 1.15, 1.17, 1.19 and 1.20. If one of these beads just floats in the liquid, then the specific gravity of the liquid is the same as that of the bead. If one bead floats and the next below sinks, then the specific gravity of



FIG. 99.—Accumulator hydrometer.

the liquid must be between these two, and so on. Where the beads cannot be easily seen (as in the case of an accumulator with a wooden cell) sufficient of the acid can be withdrawn by placing the thumb over the opening at the top of the instrument, and the position of the beads then observed.

Again, a form of hydrometer which is recommended for testing nickel plating solutions is called the **nickelometer**. Instructions are given that, for the solution to be at the correct strength, the nickelometer should read 8, 9, or 10 degrees as the case may be. This may be all very well under special cases, but specific gravity is not necessarily a criterion of the condition of a nickel solution. Further, in some of these instruments, examination has shown that the degrees roughly corresponded with those on the Beaumé scale, and the Beaumé hydrometer would serve exactly the same purpose, besides providing a much wider range and yielding actual specific gravities by reference to the table or curve.

Comparison of Results.—The following results were obtained by the foregoing methods on the same solution. They should be referred to the specific gravity bottle method as being most accurate.

Specific Gravity Bottle Method 1.107

Pipette Method 1.105

Beaumé Hydrometer—

Reading 13.8

$$\text{Specific gravity} = \frac{147}{147 - 13.8} = \frac{147}{133.2} = 1.104$$

Twaddell Hydrometer—

Reading 21

$$\text{Specific gravity} = \frac{(21 \times 5) + 1000}{1000} = \frac{1105}{1000} = 1.105$$

CHAPTER XII

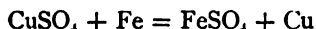
Deposition of Copper

Simple Methods.—Of all the metals, copper is the most easily and largely deposited. Numerous compounds are available, and good deposits can be obtained from the sulphate, nitrate, chloride, acetate, cyanide, etc. Being an electro-negative metal, it is readily deposited by simple immersion from these compounds—the cyanide excepted—by positive metals like zinc and iron. Copper was the first metal to be deposited on the large scale, and numerous simple experiments were being made with it over a century ago. These were made with voltaic cells of a very simple order, but the results led to work on a much more important scale, and to-day no less than half a million tons of this metal are deposited annually in the process of electrolytic refining.

Deposition by Simple Immersion was a process largely practised at one time. Now it is quite unimportant. Cheap iron goods can be and are coppered by first pickling in a weak oil of vitriol ($\frac{1}{2}$ –1 lb. per gallon) and subsequently vigorously shaking up in a barrel containing sawdust moistened with a weak solution of bluestone containing—

Bluestone	2–4	} ozs. per gallon.
Oil of vitriol	1–2	

The chemical action is as follows :—



Copper is deposited, but at the expense of the iron. Two objections to this method of depositing metals are—

(1) The deposit is none too adherent, as it is produced on a surface which is suffering chemical corrosion.

(2) The deposit must of necessity be thin and cannot go beyond a complete covering, for the iron is then no longer exposed to precipitate more copper.

The process has, therefore, a very limited application.

Single Cell Method.—What is called the “single cell” process involves the generation of an electric current and

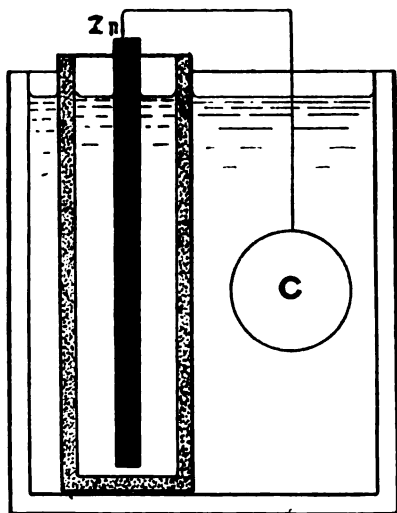
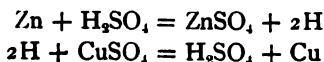


FIG. 100.—Single-cell deposition.

deposition of copper in a single piece of apparatus. Reference to the description of the Daniell cell on p. 7 will show that this actually occurs in the cell, for an essential part in the reaction is the deposition of copper on the copper cylinder or containing vessel used. For more practical purposes the copper vessel may be replaced by a glass or stoneware jar containing the bluestone solution. A piece of brass to be plated is suspended in this solution by a copper wire attached to the zinc rod which stands in the acid (see Fig. 100).

Deposition of copper now proceeds, the zinc dissolving to an equivalent extent in the acid thus—



The sulphate solution thus becomes impoverished and requires the addition of bluestone. Instead of brass or metallic articles, moulds of non-conducting materials like wax or gutta-percha may be used, but these must first have been rendered conductive by blackleading, and be attached to the zinc rod by a copper wire which runs round the mould. The deposition of copper commences at this wire and gradually covers the mould. This type of deposition presents more interest historically than industrially.

Deposition of Copper.—When an external current generator is employed, the name of “battery” or “dynamo” process has been given. These are unnecessary terms, as the current from batteries and dynamos is exactly the same, and if of the same strength, deposits the same amount of metal per ampere-hour.

The solution in common use is of a composition which admits of wide variation. Copper *can* be deposited from any weak solution of sulphate, but for good results the following solution is employed :—

Sulphate of copper ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	. . .	2 lbs.
Oil of vitriol (H_2SO_4)	$\frac{1}{2}$ –1 lb.
Water	to 1 gallon.

The sulphate of copper is the essential constituent. Oil of vitriol is an extremely desirable one, as it considerably diminishes the resistance of the solution and thus facilitates deposition. In making up a small bulk of solution the salt may be dissolved in warm water, and after cooling, the acid carefully added and the bulk made up with water. On the larger scale the capacity of the tank is first calculated and most of the water added. The weighed salts can now be suspended in the water by canvas bags, or perforated stoneware

baskets, when solution is readily effected without further trouble. If the full quantity of water is first used, the salts when dissolved will bring the specific gravity up to 1.12 (16° B. or 24° Tw.), and the addition of $\frac{1}{2}$ lb. acid per gallon will further increase the specific gravity to 1.14 (18° B. or 28° Tw.). For rapid deposition the solution can be somewhat further strengthened, but this is not necessary for most purposes.

Reactions during Deposition.—Copper can be deposited without the presence of acid. The action simply stated is—

(1) The copper sulphate produces copper (Cu) and SO_4 ions.

(2) The copper ions move towards the cathode and copper is deposited upon it. The SO_4 ions migrate to the anode, and combining with the copper form CuSO_4 . The deposition of copper is therefore not accompanied by a change of composition of the bath, and a solution may be worked continuously for years without requiring the addition of more bluestone.

(3) The action is facilitated by the presence of the acid. What part is played by the acid? This produces H and SO_4 ions. The SO_4 ions move to the anode and there form CuSO_4 . The H ions move to the cathode and there they turn out copper:— $2\text{H} + \text{CuSO}_4 = \text{H}_2\text{SO}_4 + \text{Cu}$.

If there is no CuSO_4 at the cathode, copper cannot be deposited, and the object of agitation is to maintain a good supply of copper at the cathode ready for deposition by the heavy currents which may be used.

E.M.F. required.—This, again, is very variable according to circumstances. Suppose it is required to maintain a C.D. of 10 amperes per square foot. To do this, the P.D. at the vat terminals may be for a given set of conditions, say, 0.5 volt. This P.D. will need to be—

(1) *Increased*—

- (a) if the plates are further apart,
- (b) if the solution is weaker,
- (c) if the solution contains less acid,

- (d) if the solution is cooler,
- (e) if the anodes are smaller,
- (f) if the connections are poor.

(2) On the other hand, a *lower P.D.* will be necessary when—

- (a) a stronger solution is used,
- (b) the solution contains more acid,
- (c) the temperature of the solution is raised,
- (d) large anode surface is used,
- (e) contacts are improved, and
- (f) plates are brought nearer.

These last conditions should therefore be aimed at, within reasonable limits, but it will be seen that any figure stated as the necessary P.D. is very dependent upon many circumstances. Where a voltmeter is being used, the best conditions should first be obtained and the P.D. required to maintain a good rate of deposition ascertained by experiment and adhered to as closely as possible.

Another point, however, deserves particular notice, viz. the solubility of the anode. An ideal anode loses as much metal as is deposited on the cathode. Usually this is a condition not easily attained, but one which obtains most readily in an acid copper solution. If such a solution were worked with a carbon or platinum anode (both of which are insoluble even under the influence of the current), very little current could be got through a vat with a P.D. less than 1.25 volt. The decomposition of the sulphate of copper would require energy represented by this E.M.F., but if the anode behaves ideally, then energy is there set free to the same extent as that absorbed in the decomposition, and thus, as far as the actual decomposition of copper sulphate is concerned, no E.M.F. is required, and the P.D. which must be maintained represents the force employed in overcoming resistance without chemical decomposition. Thus the more soluble the anode the lower the E.M.F. required, while in the extreme case of

the Daniell cell we have a very soluble anode zinc, which, in dissolving, generates an excess of E.M.F. to the extent of 1.08 volt.

Current Density and its Safe Limits.—Current density has been referred to as the current per unit area, usually in amperes per square foot. Imagine a sheet of metal 1 foot square in the bath and receiving on one side only, a current of 10 amperes. A particular kind of deposit is obtained. If it is required to reproduce this kind of deposit on—

2 square feet, then 2×10 amperes must be used.

10 " " 10×10 " " "

In every case the same kind of deposit will be produced when—

$$\frac{\text{Current used (amperes)}}{\text{Area (square feet)}} = 10^1$$

If plain surfaces were dealt with, then we might readily compute their area, and calculate the current. The areas with which an electroplater has to deal, however, are not of such a regular order. They are not easily computed, as they vary so much in size and shape. But whatever approximate computation can be made, by measurement or by experience, should be made, and the current adjusted accordingly.

The limits of current density will then depend on several conditions.

(1) Character of deposit required. A smooth deposit necessitates low C.D., and time must be allowed to produce the necessary thickness.

(2) A moderately rough but tough deposit demands a higher C.D., and a shorter time will be required to produce a given thickness.

(3) Too high a C.D. produces a dark and powdery deposit, especially on the edges and prominent parts of the work. This must, of course, be avoided.

¹ In future all current densities expressed will refer to these units, viz. amperes per square foot.

(4) Strong solutions allow a higher C.D. to be used without "burning" than weaker ones.

(5) Moving solutions, continually bringing a fresh supply of copper up to the cathode, likewise allow a higher C.D. to be used. This means that more current can be put through a single vat, or more metal deposited from a given-sized tank, or, in other words, a smaller-sized plant for a given output of copper. This is of great importance where copper is being deposited on the large scale.

Using the solution already stated, the following table gives approximately the kind of deposit obtainable with different current densities. Note that they are only approximate, for very different results would be obtained if, on the one hand, deposition was allowed to proceed for the same time—with different amounts of copper in each case—and, on the other hand, the same amounts of copper put on—in, of course, different times. In each case the area was $\frac{1}{90}$ square foot with the same anode area.

TABLE XII.

EFFECT OF CURRENT DENSITIES ON COPPER DEPOSITS. STATIONARY SOLUTION.

C.D.	Time.	Character of deposit.
2	60 mins.	Coarse crystalline.
5	24 "	Finer "
10	12 "	Finely granular
15	8 "	" " very good.
20	6 "	Excellent.
25	5 "	" "
30	4 "	Slightly burnt at corners.
35	3.5 "	All edges burnt.
40	3 "	Badly burnt.

It will be seen that at a C.D. of 40, a decided burning occurred. The experiments from this point were then repeated with the solution maintained in gentle motion by blowing a stream of air through the electrolyte.

Results—

TABLE XIII.

EFFECT OF CURRENT DENSITY ON COPPER DEPOSIT. MOVING SOLUTION.

C.D.	Time.	Character of deposit.
10	60 mins.	Fine grained deposit.
20	30 "	" "
40	15 "	" "
60	10 "	" "
100	6 "	Coarser grains.
120	5 "	Still coarser.
140	4 "	Corners burnt.
160	3 "	Edges burnt.
180	3 "	Badly burnt.

In each case polished cathodes were used. Moreover, this C.D. can in some cases be pushed to a much higher figure—say, from 200 to 250—without any ill effect, but these cases are exceptional and not the rule. The usual C.D.'s employed are from 10 to 40 for stationary solutions, and up to 100 or 150 for agitated baths.

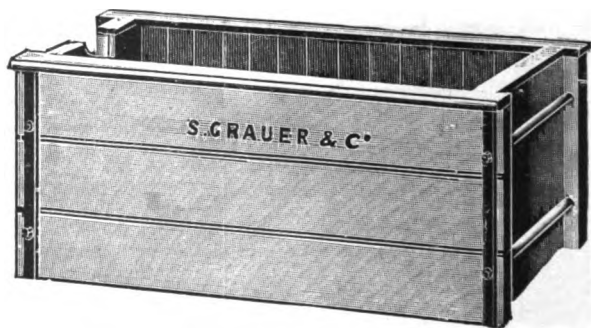


FIG. 101.—Lead-lined vat.

Vats.—Most ordinarily, wooden vats lined with lead with burned or autogenously soldered joints are used (Fig. 101).

Glass and earthenware vessels are available on the smaller scale, while well-pitched wooden tanks are sometimes used, and even tanks of slate slabs firmly bolted and cemented. Iron tanks are, of course, unsuitable, and enamelled iron is undesirable, as the disappearance of a little enamel—quite an easy matter, by the way—would result in corrosion and irreparable leaking at that place.

Preparation of Work.—Though the ordinary copper bath contains free acid, which acts as a cleansing agent and is instrumental in removing films of oxides which may form subsequent to the cleansing processes, no less care must be exercised in the preparation of the work previous to its introduction into the bath.

(a) Brass, German silver, and similar metals, if rough from casting or manufacture, will first require pickling in a weak or old dipping acid, and scoured to remove the loosened oxide. Parts may then be burnished or polished, and grease subsequently removed by potash. Any stain thus imparted may be removed by acid dipping in the case of dull work or a weak cyanide dip in the case of polished work. After thorough rinsing, the work is introduced into the bath and examined after a short time. If the deposit is not uniform, the defective portions are rubbed with sand or pumice, rinsed, and re-immersed. When satisfactory, deposition may be allowed to proceed for a half to three hours according to requirements. Then, after removing and rinsing well, the work is dried in sawdust. The deposit may subsequently be polished, if necessary, or lacquered, or, after rinsing and previous to drying, scratch-brushed, and lacquered after drying.

(b) Positive metals like iron, zinc, tin, lead, Britannia metal, and pewter require a preliminary covering of copper from the cyanide solution (see p. 181). This preliminary deposit must be absolutely perfect. The slightest imperfection will be apparent at once when the work is introduced into the acid bath, and becomes more obvious as deposition proceeds, and leads to stripping.

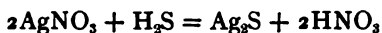
Coppering Non-conducting Surfaces.—Non-conducting materials like wood, wax, cloth, guttapercha, clay, plaster, leaves, and flowers, etc., may be coated with copper after first receiving a covering of conducting medium. Such substances are graphite, plumbago, or blacklead, finely divided metals and metallic sulphides.

The Use of Graphite is considerable for electrotyping purposes. Moulds in wax, guttapercha, and various compositions readily retain a layer of blacklead applied by gently brushing with this material. For electrotyping purposes only the finest grades should be employed. The brushing may be done by hand or machine, and any excess of blacklead should be washed off with a sharp stream of water. Similarly, clay, earthenware, plaster, etc., may be first soaked in linseed oil, to render them impervious to the solution, and allowed to dry. The skin of dried oil is then sufficient to retain a coating of plumbago when applied with a soft brush.

Metals are used in the finely divided form as bronze powders. These may be applied in the same manner as graphite, and may sometimes with advantage be mixed with this substance. Further, the surface of the non-conducting substance may be coated with copper thrown out from a sulphate solution by iron filings. Thus a blackleaded wax or guttapercha mould is placed face upwards in a solution of copper sulphate. Iron filings are sprinkled upon it, and by their contact with the graphite, form innumerable little voltaic centres, at and around which copper is deposited, producing a more or less perfect film. After rinsing off the filings and introducing into the bath, copper may be deposited at once over the whole of the surface instead of gradually spreading over the mould and producing an uneven layer, as would be the case in a blackleaded mould. Metallic films may also be produced by covering the non-conducting surface by a metallic compound painted over it, and subsequent chemical reduction to metal. This is particularly desirable in the case of delicate work like leaves and flowers, which would not stand even light

rubbing. Such articles may be painted with, or dipped in a weak solution of silver nitrate (about 5 grams per litre). The silver nitrate retained would, in course of time, become reduced to the metal, but this can be considerably hastened by using a reducing agent. Such a solution is that produced by dissolving phosphorus in the proportion of 1 gram to 20 c.c. of carbon disulphide. The solution is highly inflammable, and if upset and allowed to dry might spontaneously ignite combustible materials. It should therefore be prepared and used with the utmost care. If applied to the silver nitrate the metal is at once formed. In using this solution, however, it is more usual to apply the phosphorus solution first, and after careful drying immerse in the silver nitrate solution and allow to dry, when the silver appears as a dark grey film. Such a film at once takes a coating of copper when introduced in the bath.

Metallic Sulphides are, as a rule, good conductors when compared with other metallic compounds, though very poor when compared with the metals. A film of silver sulphide can be easily produced on a non-conducting surface by painting on, or immersing in, the weak silver nitrate solution and allowing to dry. The article is then exposed to sulphuretted hydrogen, when according to the equation—



a layer of silver sulphide is formed. The sulphuretted hydrogen may be prepared under a glass dome or bell jar by adding hydrochloric or sulphuric acid to iron sulphide (FeS), when $\text{FeS} + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2\text{S}$, and the gas is at once in contact with articles placed under the dome. After a short exposure they may be rinsed and immersed in the bath.

Parcel Coppering.—Thus far, attention has been directed to completely covering work with copper. Partial deposition, according to taste and design, can be readily effected, and is, in the case of copper, called **parcel coppering**. Starting, for example, with a plain brass plate, the process comprises the following stages :—

(1) The plate is first thoroughly cleaned for deposition, and dried.

(2) A design is then painted upon it by means of a varnish which will withstand the solution. For the acid copper bath, asphaltum varnish is quite serviceable. For hot and cyanide solutions, best copal varnish coloured with a little chrome, yellow or red, and thoroughly dried, is necessary. Many other compositions are also in vogue.

(3) After the varnish is dry, the plate is suspended in the solution, and on passing the current the unvarnished parts receive a coating of copper.

(4) When a sufficient thickness has been obtained the work is removed, rinsed, and roughly dried. The varnish is now removed by means of turpentine, when the original design appears in brass side by side with the deposited copper.

(5) Final cleaning, scratch-brushing, burnishing, polishing, etc., and lacquering complete the process.

It will be at once seen that, applied on different forms of artistic brass work, a wide variety of effects may thus be produced with dead and burnished brass, and dull deposited and polished copper, and the range of artistic effect is considerably increased when methods of metal colouring, such as are described in Chapter XIX., are further applied.

Rapid Copper Deposition.—It has been shown that under ordinary conditions a C.D. of 40 amperes cannot be safely exceeded. Many applications of deposition, however, demand a quicker rate, and this becomes possible in an agitated bath. The methods will be enumerated without detailed description.

Stirring may be accomplished by—

(A) Movement of the electrodes.

(B) Movement of the electrolyte.

A. Movement of Electrodes.—To do this the whole of the conductors, bars, and electrodes are mounted on a frame capable of slight reciprocal motion, the motion being

imparted by a small eccentric actuated by a shaft running close to the vat or vats.

B. Movement of Electrolyte.

(1) **Use of Paddles.**—These stirrers consist of several wooden paddles attached to a vertical spindle and rotated by means of a small pulley. This can only agitate below the electrodes or between them when they are a good distance apart. A better method is that in which the paddles are actuated from the side of the bath and move between the electrodes. The motion may be produced by the intermittent attraction of the paddles by an electromagnet intermittently excited.

(2) **Agitation by Air** is a simple and effective method. Air under pressure is forced through the solution by means of a perforated lead pipe at the bottom of the vat. A slight pressure from a pump is all that is required. Such a pipe should stand a little above the bottom of the tank in order that unavoidable sediment may not be disturbed.

(3) **Circulation in a Series of Tanks** is often required, and may be obtained by arranging the vats in step fashion, and syphoning the liquid from the top vat to the next, and so on to the bottom, or even allowing an overflow pipe to conduct the solution from one vat to another, finally pumping up the electrolyte from the bottom to the top. Special acid proof pumps will of course be required.

(4) **Pumps within the Solution** or simple turbine wheels have also been used to draw the liquid from the bottom of the tank and distribute it at the top.

A better method is that in which a small and slowly acting pump sucks the electrolyte through a perforated lead pipe placed at the bottom of the tank, and drives it back again with the return stroke. In any case violent agitation is not required. What is wanted is that the cathode surface shall be continually supplied with fresh strong electrolyte to take the place of that from which the metal has been deposited.

Thickness of Copper Deposits.—It will now be convenient to show the method by which the thickness of a deposit can be calculated. In most cases deposits are too thin to be capable of easy measurement, but it may be calculated by a knowledge of two factors, viz. current density and time. A similar calculation is made in Chapter VIII., but as it is one of importance it will bear repetition. For this purpose we may take the specific gravity of copper as 8.9; that is 1 c.c. of copper weighs 8.9 grams.

Now 1 cu. ft. water weighs 62.5 lbs.

∴ 1 cu. ft. copper weighs 62.5×8.9 lbs.

And 1 cu. inch copper weighs $\frac{62.5 \times 8.9}{1728} = 0.32$ lb.

Assume a C.D. of 10 amperes for 10 hours, and deal with the deposit on 1 square foot. Denote the thickness by t'' . Then—

Volume of deposit = $12 \times 12 \times t = 144t$ cu ins.
and weight „ = $(144t \times 0.32)$ lbs.

But the weight of the deposit is also known from current and time, for—

1 ampere-hour = 1.182 gram copper
 10×10 ampere-hours = $10 \times 10 \times 1.182 = 118.2$ grams
= $\frac{118.2}{454} = 0.26$ lb.

Hence—

$144t \times 0.32 = 0.26$
 $t = \frac{0.26}{0.32} \times \frac{1}{144} = 0.00565$ inch
= $\frac{1}{177}$ inch

from which the time required to deposit a thickness of 1 inch can be obtained—

$\frac{1}{177}$ inch is deposited by C.D. 10 in 10 hours

1 „ „ „ „ $\frac{10}{177}$ „
= 1770 hours

and a proportionately shorter time will be required for higher current densities.

Applications of Copper Deposition.—Of the common metals, copper is by far the most widely deposited. For a legion of purposes it is deposited either from the acid or alkaline (cyanide) bath as a protective film for the more positive metals, and to form a base on which other deposits can subsequently be made. In the form of thicker and rougher deposits, it is utilized considerably in the processes of **electro-typing**, by the application of which reproductions of medals, statues, engraved plates, wood blocks, formes of type, etc., are made in electro-deposited copper upon moulds of non-conducting but plastic materials, such as wax and guttapercha, or of plaster of Paris, etc. Thick deposits are produced, and are stripped from the moulds on which they are made. Such deposits must be sufficiently thick to be rigid and not suffer permanent deformation on being withdrawn from the mould.

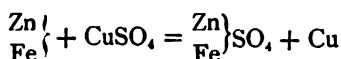
On a still larger scale, copper in the electro-deposited form is applied to the manufacture of seamless tubes. For this purpose the metal is deposited upon a rotating drum or cylinder, the surface of which has been rendered conductive. When a sufficient thickness has been deposited the cylinder is withdrawn, leaving a tube of electro-deposited copper. Such seamless tubes show remarkable mechanical properties, and have been produced of enormous size, weighing as much as 3 to 5 tons. Large cylinders are made for special purposes, and smaller ones can be opened out by cutting them through longitudinally to form sheets, or the cylinders may be drawn down to tubes of smaller diameter. The process has attained a large application. Attempts have also been made to produce wire almost directly by the depositing process. Copper articles of peculiar shapes have been made by depositing the metal on moulds made in fusible metal, which is subsequently melted away from the deposit. By far the most important application of copper deposition, however, is that of refining, an enormous amount of this metal being deposited annually in order to

ensure its purification. In this process anodes of impure copper, from 1 inch to $2\frac{1}{2}$ inches thick, and cathodes of thin sheet pure copper are used in the sulphate solution. With only a moderate current density of 10 to 40 amperes per square foot, the copper deposited is perfectly pure, some of the impurities entering into and remaining in the solution, and others falling to the bottom of the tank as a mud. This mud contains silver and gold, and these metals are extracted from it in large quantities. The refining process is carried out largely in America, where cheap electric power is obtainable from many waterfalls. About half a million tons of copper are refined annually by this method.

CHAPTER XIII

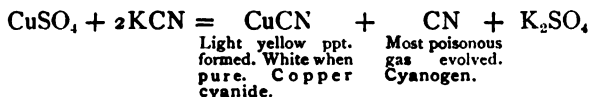
The Copper Cyanide Solution

Effect of Metals upon Copper Sulphate.—It has been shown that some metals readily decompose copper sulphate. Iron and zinc are striking examples when—

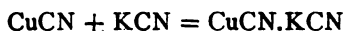


Further, both of these metals are dissolved by sulphuric acid, which is an essential constituent of the acid copper bath. It is obvious, therefore, that these metals cannot be coated successfully in this solution. Yet they are metals which, on account of their positive character and ease of corrosion, need to be protected by some less corrodible metal. Copper is a cheap metal for this purpose, and may also form the basis for metals of a more valuable and ornamental character. Some more stable compound of copper is therefore required for not only these metals, but also for depositing copper on tin, pewter, Britannia metal, etc. Other copper compounds—the nitrate, chloride and acetate—are similarly unstable and of little use for plating purposes.

Copper Cyanides.—When potassium cyanide is added to copper sulphate, the following action occurs:—



This copper cyanide is **cuprous cyanide**, **cupric cyanide**, if formed, being unstable, and therefore undergoing decomposition. Cuprous cyanide is, when pure, a white insoluble powder. The commercial compound has usually a greenish-yellow appearance. It dissolves readily in more cyanide, producing a soluble material—



This CuCN.KCN or CuK(CN)_2 is called double cyanide of copper and potassium, and is the essential constituent of cyanide copper solutions. When pure, it is white and crystalline. When crystallized from solutions containing free potassium cyanide, the crystals contain excess of cyanide. If such a solution, however, is boiled with copper carbonate (CuCO_3), then, after filtering off any excess of carbonate and crystallizing, the crystals obtained are pure double cyanide (CuCN.KCN). These are not freely soluble in water, slight decomposition into CuCN and KCN occurring, but the addition of more KCN dissolves them readily. Further, the ordinary double cyanide of commerce frequently contains this excess of KCN , as the following analyses made in the author's laboratory will show :—

	CuCN.KCN.	
	(Calculated composition.)	Bought sample (analysis).
Copper	Per cent. 40.9	Per cent. 24.3
Free KCN	0	41.5

$$\text{Now } \frac{\text{CuCN.KCN}}{\text{Cu}} = \frac{154.6}{63.6}$$

$$\therefore 24.3 \text{ Cu} = \frac{154.6}{63.6} \times \frac{24.3}{1} = 59 \text{ per cent. CuCN.KCN}$$

The composition of the commercial salt therefore becomes—

CuCN.KCN	59.0 per cent.
Free KCN	41.5 „
	<hr/> 100.5

If into a solution of this double cyanide of copper and potassium, strips of clean iron and zinc are introduced, no simple immersion deposition of copper on iron occurs, but a slight and fairly adherent film occurs on the zinc, especially when free cyanide is present. The solution is thus suitable for the deposition of copper upon the more positive metals.

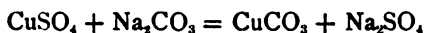
Preparation of the Solution.—Several methods may be followed, each giving a solution yielding good deposits of the metal. In no case should the cyanide be added directly to copper sulphate. Besides being wasteful in its consumption of cyanide, it is dangerous from the amount of poisonous cyanogen gas evolved.

Determine first the weight of metal which the solution shall contain. The amount may vary considerably up to 6 or even 8 ozs. of metal, equivalent to $1\frac{1}{2}$ or 2 lbs. of sulphate per gallon. Such strong solutions are not frequently employed, one containing 4 ozs. of metal being sufficiently strong for practical purposes. The following methods may then be followed :—

Method No. 1.—Dissolve the copper sulphate in water, and add, a little at a time, strong ammonia solution, shaking after each addition. A green precipitate of copper hydrate $[\text{Cu}(\text{OH})_2]$ is formed, and, on the addition of more ammonia, this dissolves completely, forming a clear blue solution. Dissolve separately one and a quarter times as much potassium cyanide as bluestone used, and make a strong solution. Add this to the blue copper solution, shaking after each addition. Gradually the intense blue colour is lost, and finally disappears entirely. The copper is then completely converted into the double cyanide. The volume and hence the weight

of cyanide used can now be observed, and a further quantity of about one-quarter of that already used is added. The solution is then made up to the bulk intended, and is ready for use. The following figures for 1 gallon were obtained in an experiment: 1 lb. bluestone dissolved in 2 pints of water; ammonia (strongest solution) required to produce the intense blue solution = 16 fl. ozs.; $1\frac{1}{4}$ lbs. good cyanide dissolved and made up to 2 quarts; 64 fl. ozs. added to decolorize the blue solution, and a further 16 fl. ozs. added for free cyanide. Water is now added to make 1 gallon, and specific gravity at 15° C. = $1.140 = 28^{\circ}$ Tw. The same thing carried out for a weaker solution was as follows: 8 ozs. bluestone dissolved in 1 quart of water; ammonia required for blue solution = 8 fl. ozs.; 10 ozs. cyanide dissolved and made up to $1\frac{1}{2}$ pints water; 24 fl. ozs. cyanide solution required to decolorize, and further addition of 6 fl. ozs. made. Solution made up to 1 gallon, when specific gravity at 15° C. = $1.085 = 17^{\circ}$ Tw.

Method No. 2.—The precipitating work of the ammonia can be effected by a cheaper material, viz. washing-soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), thus—



For this purpose prepare a solution of washing-soda ($1\frac{1}{4}$ lbs. for every pound of bluestone) and add to the copper sulphate solution. This quantity will effect complete precipitation. Now add much more water and allow to settle. Pour away the clear and almost colourless liquid, and add more water to the precipitate. Stir, allow to settle, and pour away again. This washes away the Na_2SO_4 , which will serve no useful purpose in the solution and is therefore better left out. The washed precipitate may now be dissolved in a solution of potassium cyanide, an additional amount of cyanide being added for free cyanide as before.

Example.—One gallon solution to contain 2 ozs. metal. Eight ozs. bluestone dissolved in 1 quart water, 10 ozs. washing

soda dissolved in 1 pint water and added to the copper solution—with stirring. After washing, 32 fl. ozs. of a solution containing 10 ozs. cyanide in 1 quart served to dissolve the green precipitate, and 8 fl. ozs. were further added. Solution made up to 1 gallon.

Method No. 3.—Prepare a solution of potassium cyanide containing about $1\frac{1}{2}$ lbs. per gallon. Set aside one-quarter of this solution. The remainder is now warmed, and copper carbonate (which may be purchased or prepared as in Method No. 2) is added. At first it dissolves quite easily, but as the solution acquires more copper, the reaction takes place more slowly. When no more carbonate is dissolved, allow to settle (about 12 ozs. of the carbonate will dissolve). Pour off the clear liquid as completely as possible, and filter the remainder, adding the filtered solution to the clear liquid which has been poured off. Now add the cyanide solution originally set aside, and the solution is then ready for use.

Many other methods are available, but the above are sufficient. The addition of other materials is to be avoided, solutions being kept as simple in their composition as possible.

Reactions on Electrolysis.—The essential constituent of the above solutions is the double cyanide of copper and potassium (CuCN.KCN). When the current passes through the solution the following actions occur:—

- (1) Copper does *not* move towards the cathode.
- (2) The cation is potassium (K).
- (3) The anion (moving towards the anode) is the complex group Cu(CN)_2 .
- (4) When K reaches the cathode it turns out copper by what we may regard as a simple chemical action—



free potassium cyanide being formed.

- (5) When Cu(CN)_2 reaches the anode it combines with copper and forms the insoluble single cyanide (CuCN).



This single cyanide is only soluble in KCN, and the anode in the absence of free cyanide becomes coated with the insoluble cyanide, which considerably hinders the passage of the current. Free cyanide keeps the anode clean by dissolving the single cyanide as fast as it is formed.

(6) Hence it is seen that while KCN is being formed at the cathode, it is really required at the anode. Obviously, then, stirring will facilitate the mixing up of the free cyanide, and warming will also be of great assistance in dissolving the single cyanide. If the solution is both stirred and warmed, the amount of free cyanide necessary is reduced to a minimum, and this favours the deposition of metal more easily with the production of much less gas. Under these conditions, with quite a little free cyanide, the anodes can be kept perfectly clean, and in fact this may occur in the absence of a measurable amount of free cyanide.

These points are of great importance in the uniform working of the bath, and it is only by maintaining clean anodes that the metal can pass into solution as fast as it is deposited, and thus maintain the metal content of the solution.

E.M.F. required.—This is governed almost entirely by the conditions previously mentioned. The E.M.F. required for a cyanide copper solution is variously stated to be from 3 to 5 volts. If, however, the above conditions are realized, the E.M.F. required is very low, amounting to not more than 0.5–1 volt. It is dependent also upon the current density to be used, but a C.D. of 20–30 amperes per square foot is quite easily maintained in a warm solution, stirred moderately, with only a small amount of free cyanide. In a cold solution at rest and containing no free KCN it is quite possible for the anodes to become so perfectly coated that the current will fall to zero. This is shown in the following figures.¹

¹ *Trans. Faraday Soc.*, vol. v. p. 175.

TABLE XIV.

ILLUSTRATING BEHAVIOUR OF ANODES IN THE SOLUTION WITHOUT
FREE CYANIDE.

SOLUTION COLD.

I.			II.		
Time from start.	Amperes.	Volts.	Time from start.	Amperes.	Volts.
1 min.	1'35	3'18	1 min.	1'61	3'22
2 "	1'32	3'21	2 "	1'59	3'26
3 "	1'30	3'28	3 "	1'57	3'32
4 "	1'26	3'37	4 "	1'51	3'44
5 "	0	3'51	5 "	1'40	3'70
			6 "	1'10	4'45
			7 "	0	4'8

TABLE XV.

SOLUTION WARM.

III.			IV.		
Time from start.	Amperes.	Volts.	Time from start.	Amperes.	Volts.
1 min.	1'43	2'86	1 min.	1'66	2'98
2 "	1'42	2'86	2 "	1'64	3'00
3 "	1'41	2'87	3 "	1'65	3'02
4 "	1'39	2'90	4 "	1'61	3'03
5 "	1'39	2'90	5 "	1'61	3'05
6 "	1'39	2'90	6 "	1'60	3'07
7 "	1'38	2'93	7 "	1'60	3'11
8 "	1'38	2'93	8 "	1'58	3'13
9 "	0		9 "	1'57	3'17
			10 "	1'54	3'22
			11 "	1'50	3'30
			12 "	0	

The accompanying curves (Fig. 102) embodying these results make the matter more obvious. They clearly show that even with higher currents producing greater amounts of the insoluble cyanide, the formation of the perfect film which reduces the

current to zero is delayed. The application of these principles will be apparent. The figures and curves are for a solution containing no free cyanide and at rest. These are conditions, therefore, to be avoided.

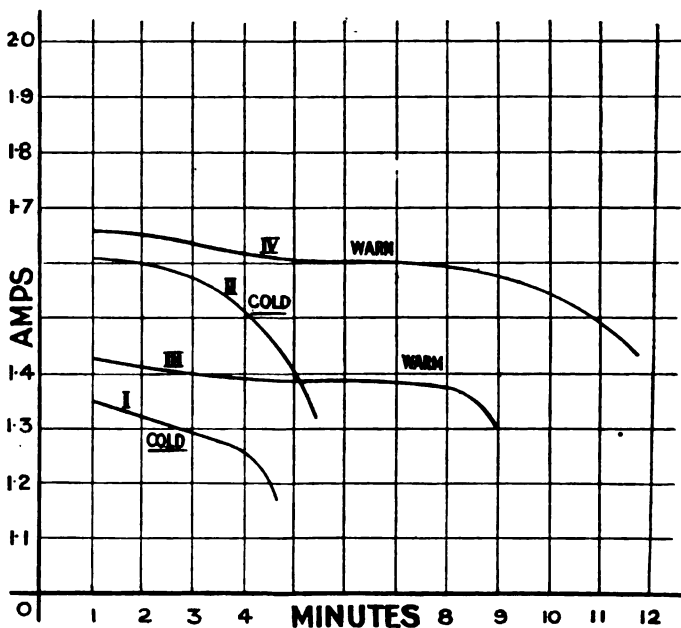


FIG. 102.—Showing formation of insoluble film on anode.

Quantitative deposition of Copper from the Cyanide Solution.—It must always be a matter of interest and importance to know the maximum amount of metal which can be deposited from a plating solution per ampere-hour. We can determine this experimentally for the cyanide bath by arranging a small bath in series with a copper voltameter, making a series of experiments and weighing the deposits. Obviously the very best conditions must be aimed at. They are—

- (1) Strong solution.
- (2) Warming and stirring.
- (3) Minimum free cyanide.
- (4) Only a moderate current density.

The copper voltameter is of course supposed to combine the best conditions for that solution. The following results were obtained in such experiments :—

Experiment.	Copper deposited.		Cu (from cyanide) Cu (voltameter)
	Voltameter.	Cyanide solution.	
1	0·2053	0·3450	1·68
2	0·2460	0·4600	1·87
3	0·1586	0·3024	1·91
4	0·2916	0·5694	1·96

It is thus seen that the copper from the cyanide solution approaches but does not exceed twice that from the voltameter (acid solution). It would almost seem as though, on the principle that such chemical quantities are simply related, the proportion ought to be *exactly* twice. Now the fact that deposit stands in a solution capable of dissolving it slightly, prevents the exact figure being obtained. This amount of loss was therefore determined. The results then appear—

	Copper from voltameter.	Cu from cyanide.	Cu (cyanide) Cu (voltameter)
Ordinary result .	0·3458	0·6870	1·98
Add loss by solution	—	0·0052	—
Corrected result .	0·3458	0·6922	2·00

Under the best conditions, therefore, the cyanide solution yields twice the weight of copper per ampere-hour as the acid solution. Under ordinary conditions, however, the proportion

would be less, as each of the following conditions are not conducive to quantitative deposition :—

- (1) Weaker solutions.
- (2) Solutions containing free cyanide.
- (3) Solutions not stirred.
- (4) High C.D.

Experience soon shows that a considerable evolution of gas may and does often occur. If gas is evolved, then its equivalent of metal is not being deposited; moreover, much "gassing" may occur without producing a "burnt" deposit. In this solution at any rate, therefore, the cause for burning must be sought in other directions.

Preparation of Work.—The chief metals plated in this solution are iron, zinc, lead, tin, pewter, and Britannia metal, and usually copper is deposited on these metals as a preliminary coating for other metals. The cyanide solution is also used where it is necessary to deposit a smooth film of copper upon brass. In any case the acid copper deposit is dull and needs polishing. The cyanide copper deposit may, however, be kept quite bright.

Different metals naturally require different kinds of treatment previous to deposition. Iron and steel may be polished and afterwards potashed and lightly scoured with fine pumice, and at once introduced into the bath. The free cyanide in the solution possesses cleansing properties, which, while an advantage, must not be relied upon. Work should be thoroughly cleaned before being placed in the solution. Cast iron, if not required polished, may be first pickled in a weak sulphuric acid (1-20), rinsed, and well scoured with sand.

Zinc may require only a brief treatment in potash as the metal is freely soluble in the alkali. It is then scoured and passed through sulphuric acid (1-10), and after a further scouring, rinsed and placed in the vat.

Tin does not require an acid dip. It is quickly passed through the potash, and after rinsing, scoured and transferred to the solution. Lead, pewter, and Britannia metal need similar treatment, no acid dips being required. When such

work containing soldered joints is coppered, some difficulty may be experienced in obtaining a ready deposit on the solder. Special attention should therefore be given to such places, and as soon as any difficulty is experienced the work should be removed, scoured, and put back into the bath. The inside of a vessel is a little difficult, but this can best be done by filling the vessel with the warm depositing solution, joining it to the negative lead and introducing a small copper anode. Deposition can then be completed in the bath as usual.

For thick deposits of copper the work is now removed, rinsed, scratch-brushed, thoroughly rinsed again, and transferred to the acid bath. Especial care, however, must be taken to ensure a perfect coating in the cyanide bath, and also that the work is perfectly rinsed. If the coating is imperfect, corrosion begins at the imperfections and continues under the deposit, leading to stripping. If the rinsing is incompletely done, the acid reacting on the cyanide solution produces a decided stain.

Character of Deposit.—The cyanide deposit differs from the acid deposit in several important respects. It is usually brighter, and on a polished surface needs little finishing. Hydrogen may be deposited freely without burning the deposit. Hence when burning occurs it is more usually attributed to the presence of traces of oxide or other basic compounds in the deposit. Evidence for this is forthcoming in the fact that the addition of substances in which copper compounds are freely soluble, such as cyanide, ammonia, sodium bisulphite, etc., considerably diminishes the burning. Sometimes with low C.D. a dark red deposit is obtained, especially in cold solution. Addition of cyanide and increase of current often overcome this difficulty.

The cyanide solution of copper can be conveniently contained in a lead-lined wood vat if worked cold, but it is much preferable to use wrought-iron tanks with convenience for external heating by gas, or internal heating by waste steam, which may be passed through an iron or lead coil so that the condensed water may not pass into the solution.

CHAPTER XIV

Deposition of Nickel

History and Utility.—From the time of the introduction of nickel plating by Adams in 1866, great advances have been made in the methods by which the metal is deposited and the purposes to which it has been put. Its value as a covering for other metals is due partly to the brilliant lustre which may be imparted by polishing, partly to its durability in contact with the atmosphere, suffering little tarnishing, and partly to its hardness and resistance to wear and tear. In many ways this process of deposition has been applied with signal success.

The Solution.—The solution which is most commonly used has the following composition :—

Nickel ammonium sulphate (double nickel salts)	12 ozs.
$(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	
Water	1 gallon.

Just this—and nothing more. The double nickel salt may be bought or prepared. It is none too soluble in water, but the solubility is much increased on warming. To prepare a solution the crushed salt should be dissolved in warm water, and the solution transferred to the tank already containing sufficient water to prevent crystallization. If the solution prepared is not clear it should be filtered. A simpler method is to put the water into the vat and suspend the salts in canvas bags or perforated baskets. Where time is no object, this course is easy. The solution in any case is easily made.

Such a solution has a specific gravity of 1.045 (= 6° B. and

9° Tw.). It will not take up much more salt, and should more salt be dissolved on a warm day, it may be thrown out again upon a cooler day. The solution should be neutral, not affecting either kind of litmus. The necessity for frequent testing will be shown later.

Further Additions to the Solution.—While the above solution obtains an extensive use, many modifications have been made or suggested. The need of modification arises from the following considerations :—

(1) The above solution, while nearly saturated with respect to double salts, contains only 1·8 ozs. of metal per gallon. The acid copper bath contains nearly 8 ozs. The rate of deposition of nickel is thereby limited.

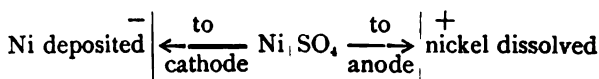
(2) No sulphuric acid can be added to increase the conductance. Nickel cannot be deposited in the presence of much acid, and is not satisfactorily deposited in the presence of only small quantities.

(3) There is some tendency for a green slime to form on the work, and mineral acid cannot be added to prevent this.

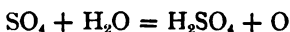
Modifications in the formula are therefore made with the object of increasing the nickel content and raising the limit of C.D., increasing the conductance of the bath, and preventing the formation of slime. One plater increases the strength of his solution by the addition of single nickel salt ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$), which is distinctly more soluble than the double salts. Others, however, maintain that a deposit from such a solution is not so white. Further, common salt and sal-ammoniac have been added to increase the conductance, and incidentally the whiteness. Others, however, maintain that this induces excessive corrosion of the anodes. To prevent the formation of green slime at the cathode, weak acids, like boric or citric, have been added. Probably not much is to be gained by so doing. While some platers, over a wide experience, insist on the necessity of the occasional addition of more nickel salts—preferably single, others, over a similar wide experience, find that this is not so. One feels almost tempted to say, "Every

man to his own opinion." For our part, we should not advocate the addition of any substances other than the original double salts, save perhaps an occasional addition of ammonia to counteract inadequate anode action and the formation of acid, and additions of single salts to increase the nickel content which may become reduced owing to inefficient anode solution.

Chemical Action in Nickel Plating.—If we start with double salts, we have two salts in the solution, viz. ammonium sulphate and nickel sulphate. Both substances may be decomposed thus—



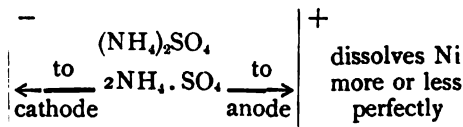
Now, nickel is not so readily dissolved as copper. Hard-rolled nickel resists the corrosive action of the SO_4 , which then acts on water thus—



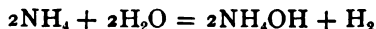
makes solu- gas evolved
tion slightly at anode
acid

Gas at the anode means imperfect anode solution and the formation of acid.

Similarly, ammonium sulphate behaves as follows :—



when



gas at
cathode

This ammonium hydrate (NH_4OH) produces a green precipitate with the nickel compounds, and this accounts for the slime which sometimes occurs. Fortunately, however, the above action occurs to only a very limited extent. The presence

of a small quantity of sulphuric acid, sufficient to be just detected by litmus, would appear not to be injurious, but have the advantage of at once neutralizing any ammonia which may be formed at the cathode.

Thus the chemical action in a nickel bath is by no means so simple as that of the acid copper, and much depends upon the solubility of the anode.

Electrical Conditions for Nickel Plating.—Nickel plating is usually regarded as requiring rather a high E.M.F. It is a practice commonly adopted to momentarily use a high E.M.F. until the work is just covered with nickel, and then to reduce the E.M.F. This is called "striking," and 5 to 6 volts may for a few moments be used for this purpose. The E.M.F. is then quickly reduced to 2 to 3 volts, or even less, to put on the bulk of the metal. Now it is the P.D. between the terminals, or E.M.F. used (together with the resistance of the bath), which determines the current density. But, as with copper, the C.D. permissible is a very elastic figure, depending upon many conditions such as those stated under copper. Any figures here given must therefore be accepted with some amount of reserve. With a solution of ordinary strength the following figures (Table XVI.) were obtained in a series of experiments :—

TABLE XVI.

EFFECT OF CURRENT DENSITY IN NICKEL BATH.

Experiment.	C.	C.D.	Remarks.
1	0.25	5	Good.
2	0.50	10	"
3	0.75	15	"
4	1.0	20	Slight burning on corners.
5	1.25	25	Burning on edges.
6	1.50	30	Very badly burnt.

In a solution to which single salts had also been added the following improved results were obtained :—

TABLE XVII.

EFFECT OF CURRENT DENSITY IN NICKEL BATH WITH SINGLE SALTS ADDED.

Experiment.	C.	C.D.	Remarks.
1	0.25	5	Good deposit.
2	0.50	10	Very good deposit.
3	0.75	15	" " "
4	1.0	20	" " "
5	1.25	25	Slight burning.
6	1.50	30	Decided burning.
7	1.75	35	Badly burnt deposit.

These results were obtained in experiments over a short time. For longer deposition the permissible C.D. would need to be appreciably reduced.

A little experience will soon show an intelligent plater, who uses both ammeter and voltmeter, the conditions which best suit his bath. Too high a C.D. produces a dark and dull deposit, beginning, as a rule, on the edges—a deposit which will not withstand the finishing process without stripping.

Character of Nickel Deposit.—Deposited nickel is hard and not usually scratch-brushed. As polishing removes metal, the less of this is done after plating the better. Hence work should be well polished before immersing in the bath. Scratches and marks in the metal before plating will not be removed by subsequent polishing. On such a bright surface a beautiful bright and white deposit may be obtained which requires very little finishing. If the C.D. is high, this deposit becomes dull, and can only be rendered lustrous by more severe polishing which removes metal, while an excessive current produces a black powdery deposit, especially on the edges. Careful control of the current conditions is essential for success.

Vats may be of lead-lined wood on the large scale. The solution is perfectly harmless, and almost non-corrosive.

Anodes demand particular attention. These may be cast or rolled. Rolled metal is harder and more compact than cast metal. The advantages and disadvantages of both may thus be enumerated :—

CAST ANODES.

(1) Must be of decided thickness, and therefore involve larger initial outlay.

(2) Being more porous, are more readily attacked in the bath. This maintains a more uniform concentration, and hence more uniform working, and gives rise to less gas at the anode.

(3) Being porous, are liable to disintegration, and therefore produce more scrap.

ROLLED ANODES.

May be of thin metal, therefore much lighter and of lower cost.

Hard and less soluble. This leads to the solution becoming impoverished and therefore less uniform in its working.

Gas is more freely evolved owing to inefficient solution of the anode.

May be worked to very thin sheets without falling to pieces.

One so-called advantage claimed for rolled anodes is that "they last a very long time." That is the unfortunate disadvantage of rolled anodes—they last too long, and the solution suffers as a natural consequence. The kind of anode used has, therefore, a marked effect on the working of the bath.

Cast anodes are provided with holes at one or both ends, so that they may be suspended in the bath by nickel hooks (Fig. 103).

Anode and Cathode Efficiencies.

—Now, an anode should dissolve to the same extent as metal is deposited. But nickel anodes seldom behave so well, and may dissolve only very slightly, or even not at all. The following table¹ shows



FIG. 103.—Nickel anode.

¹ *Trans. Amer. Electrochem. Soc.*, vol. iv. p. 87.

the behaviour of different kinds of anodes, with varying current densities, during a series of experiments on a small scale :—

TABLE XVIII.
ANODE AND CATHODE EFFICIENCY IN NICKEL BATH.

Nickel Anode.	C.D. Amps./sq. ft.		Efficiency.	
	Anode.	Cathode.	Anode.	Cathode.
CAST. Surface ground smooth . .	4'0	2'2	46'3	75'4
CAST. Surface roughened in acid .	4'0	2'2	91'3	92'6
ROLLED	4'5	4'5	8'5	63'3
ELECTROLYTIC	4'5	4'5	12'6	61'6

From these figures, note the following points particularly :—

- (1) Cast anodes dissolve more freely than rolled anodes.
- (2) Roughened anodes dissolve more readily than smoothed ones.

Therefore the best effect at the anodes is obtained by exposing a large surface and obtaining a small current density. Again, cathode efficiencies do not immediately follow anode efficiencies. We may have for a time good cathode efficiency with poor anode solution, but in the course of time a poor anode efficiency must of necessity weaken the solution and produce a poor cathode efficiency. Much more could be said on this matter, but this, with what has already been said in Chapter VIII., must now suffice.

Preparation of Work for Plating.—Two main classes of work need separate mention—

- (1) New work.
- (2) Old work previously nickeled.

In the former the preparation for plating is usually simple. When renickeling old work, however, it is essential that all the previous nickel deposit should be removed. This is called "stripping."

Stripping may be done by three methods—

(1) Mechanically, by polishing, etc.

(2) Chemically, by dissolving in acids.

(3) Electrolytically, by making the work an anode in an old solution.

This last method fails to find application in the case of nickel. Practically the whole of the stripping of old nickeled work is done by polishing. This of course applies to surfaces which lend themselves to such treatment, and in removing the old deposit, the surface is being prepared to receive the new deposit. It is of the utmost importance that the deposit should be entirely removed. The chemical method is of limited application in the case of nickel, and involves the use of materials which dissolve away the nickel, leaving as far as possible the basis metal unaffected. The following mixture is suitable for the purpose :—

Nitric acid	1 volume
Oil of vitriol	2 volumes
Water	1 volume

The oil of vitriol is first carefully added to the water with gentle stirring. After cooling, the nitric acid may be added. The work for stripping should be dry, and should be carefully watched in order to avoid excessive corrosion of the basis metal.

After the removal of the nickel, the surface is then prepared by polishing.

The work for nickel-plating can now be divided again according to subsequent treatment. For example, copper, brass, German silver, iron, and steel may be nickel-plated without coppering; while it is best to resort to preliminary coppering in the case of zinc, lead, pewter, Britannia metal, etc. Some difference of opinion may exist in the case of iron and steel. In the early days of nickel-plating, coppering was thought to be essential, and for best work was frequently resorted to. In days of increasing competition, however,

coppering is not so frequently practised. There can be no doubt that nickeling is safer on copper than on iron and steel, but it has the disadvantage of its colour being prominent when the nickel has worn through. On the other hand, if satisfactorily applied to iron and steel, it prevents these metals from corrosion. With regard next to the omission of coppering, while the worn nickel exposes a surface of only slightly differing colour, the corrosion of the exposed iron surface is most rapid, taking place underneath the nickel deposit, and thus rapidly promoting further stripping. For coppering, the cyanide solution must be used. It may, however, be followed by the acid bath if only a dead deposit is required, or if further polishing is resorted to. This of course is the best plan, though entailing greater labour and cost. After polishing, a thorough scouring with hot potash is essential.

There is, however, an objection to putting nickel on to a finely polished surface. Adhesive deposits would better be obtained on a slightly roughened surface, and, as subsequent finishing must be applied, it is well to very lightly scour with the finest pumice powder previous to plating. Whiting has also been used to advantage for this purpose.

Deposition of Nickel.—Whatever methods of preparation are applied, the utmost care to ensure perfect cleanliness must be taken. The nickel-plating solution does not contain any constituent which, like the acid in the acid copper bath or the free cyanide in cyanide solutions, will remove slight films of tarnish which may form as the result of a momentary exposure after cleansing. To ensure perfect freedom from such films the work should be passed through a cyanide solution ($\frac{1}{2}$ –1 lb. per gallon), commonly known as the “cyanide dip.” It is then passed through at least two changes of clean water and immersed in the bath. It should then be at once coated with nickel, or “struck.” This “striking” consists of rapidly covering the work with nickel, using a current in excess of that usually allowed. Such treatment for a few

moments serves to cover the work before it can oxidize and tarnish. When completely covered, the current should be decreased, otherwise burning would rapidly occur. Throughout subsequent deposition the metal should remain moderately bright, though the original lustre will be somewhat lost. Excessive current produces a dull deposit, and on the edges a dark grey or even black powder is formed. In order to ensure uniformity of thickness of the deposit, anodes should be suspended all round the work, and should as far as possible be equally spaced from the different parts of a large piece of work. The position of slinging wires should not be too permanent, otherwise a mark may be left upon the work. When examining the deposit from time to time, the work should not be kept out of the solution for more than a few seconds. Within quite a short time an imperceptible film of oxide forms, and this may lead to stripping. In fact, it is well-nigh impossible to put upon a film of nickel which has been exposed for some time a further adherent deposit without some special treatment. Stripping is most likely to occur, and it occurs very markedly. It is for this reason that none of the old deposit should remain upon work to be replated. For the same reason, old wires for slinging should not be used again. Stripping may start from them, and may even pass to the work. This is extremely inconvenient, as nothing short of the entire removal of the nickel and a fresh start can prove satisfactory.

Dead Nickel.—A very satisfactory dull white deposit, which provides a striking contrast with the highly polished metal, may be obtained in the following manner. To start with a dull surface we may, in the case of cast work, neglect the polishing processes. On sheet and stamped work the necessary dulness may be obtained by sand-blasting. On any work a slight deposit of copper from the acid bath (using the cyanide first, if necessary) provides a surface upon which the nickel deposit produces a very agreeable result. When the coppering is resorted to, the work may be well rinsed and passed at once to the nickel bath. Subsequently the dead

nickel deposit should not be handled more than is absolutely necessary, as the presence of a finger-mark considerably diminishes the effect. Dead dipping may also be applied previous to the plating process.

Thick Deposits.—The deposits obtained from ordinary nickel solutions are thin, and any attempt at producing a thick deposit results usually in stripping. The production of thick nickel deposits has, however, received some attention with a view even to the production of nickel electrotypes. In the latter case a deposit of nickel might be produced on the mould, and when sufficiently thick could be further thickened and strengthened by a deposit of copper upon it. For this purpose only strong solutions of nickel will be of any use, and these cannot be prepared with the double salt on account of the only moderate solubility of this material. Single nickel salt, being much more freely soluble, is invariably used. Langbein recommends a solution containing 3 lbs. of single salts and $1-1\frac{1}{2}$ lbs. of magnesium sulphate per gallon, and kept slightly acid with acetic acid. The solution is more effective when hot, and for electrotyping purposes moulds must be made of materials which will not soften in the heated liquid.

In order to continue the deposition of nickel rapidly, it is obvious that the nickel content of the bath must be kept high, and this, if not effected by anode solution, must be made good by the addition of single salts. The use of ethyl sulphate or of magnesium ethyl sulphate is further recommended.

Nickeling Small Articles.—An enormous amount of work to be nickel-plated consists of small parts only, such as screws, nuts, and bolts, and small fittings. The wiring of these is slow and not satisfactory. They are therefore plated in a wire basket, such as is shown in Fig. 104. Usually they do not require a heavy deposit, but they should be shaken occasionally in order to ensure uniform deposition. In the case of somewhat larger parts, it is now common practice to plate these in a drum which is caused to slowly rotate. This rotation provides for the exposure of the whole of the

surface, and a great saving of time and labour can thus be effected.

Nickeled Stereos.—Within recent years nickeling has been largely applied in this direction. The rapidity with which stereotypes may be made, and the excellence of the impressions which are now being produced, have served to bring stereotyping forward as a rival to electrotyping. The great disadvantage, however, lies in the fact that the plates are not so durable in the press and fewer copies can be obtained from them. This disadvantage is being to a considerable extent overcome by nickel-facing the stereotypes. In doing this,

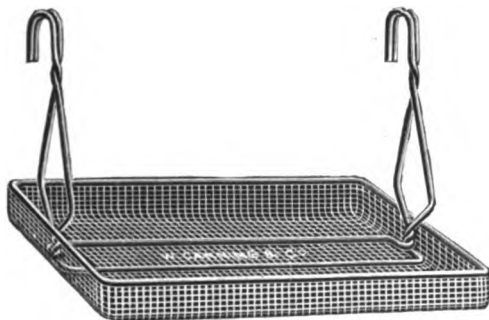


FIG. 104.—Tray for nickeling small articles.

a first rub in potash is essential, after which the plates are immersed in the cyanide copper bath to receive a thin film of that metal. After most thoroughly rinsing, the plates are transferred to the nickel bath, in which they may receive a deposit for about ten to fifteen minutes. The current density must, however, be kept low, otherwise a rough deposit would blur the impression. When correctly done, an even sharper impression may be produced and much more easily maintained during the printing process. The deposit has a great advantage also in that it is unaffected by certain coloured inks prepared from vermilion, which contains mercury.

Finishing.—The nickel deposit, while tolerably smooth,

is capable of receiving an exceptionally fine lustre. Its hardness permits this. Polishing serves to impart this lustre. In any case, however, it must be remembered that polishing removes metal, and the less done the better. This finishing is done with lime. For this purpose the best Sheffield lime is necessary. As this substance rapidly absorbs moisture from the air and becomes useless, it must be preserved in air-tight tins or jars. It may be used either as a fine sifted powder or in the lump form, when it is pressed against the finishing mop frequently during the finishing process.

CHAPTER XV

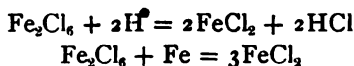
Deposition of Iron, Tin, and Zinc

Use of Iron Deposits.—The deposition of iron is carried on chiefly with the object of coating engraved copper plates for printing purposes. The unprotected engraved plate suffers much by wear, but the deposit of iron is very much harder and retains the sharpness of the impression for a much longer time. Further, when such a deposit shows signs of wear, it can be easily stripped and a new deposit put on with little trouble. The hardness, definition, and durability necessary for printing purposes may also be obtained by deposits of nickel, but much greater difficulty is experienced in removing worn deposits. In addition to its durability on account of greater hardness, a deposit of iron is advantageous by reason of the fact that it is but little affected by some of the constituents of coloured printing inks, especially those compounded with vermilion, which is a sulphide of mercury. In contact with copper, mercury is set free, and, amalgamating with the plate, at once injures the impression. With an iron coating the mercury compounds are not so easily decomposed. When through wear the first trace of red copper is seen through the iron deposit, the whole of the deposit is removed in weak acid and another coating imparted to the plate, thus considerably lengthening its life.

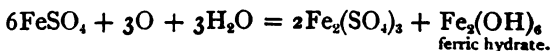
Iron Compounds available for Deposition.—Of a very large number of iron compounds few are available for use for deposition purposes.

Of the two classes of compounds, ferrous and ferric (see

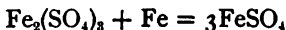
p. 273), the ferrous compounds are in greater demand. Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), or green vitriol, is similar to single nickel salts, while ferrous ammonium sulphate [$\text{FeAm}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$] is a compound of analogous composition to double nickel salts. Both of these salts may be used, and are of only moderate cost. Ferric compounds are not used. From ferric compounds a deposit of iron is not easily obtained, the ferric compound chiefly undergoing reduction to ferrous by the hydrogen or iron, thus—



A great disadvantage of ferrous compounds is the ease with which they oxidize when exposed to air. Thus ferrous sulphate solution on exposure suffers the following change:—



This ferric hydrate forms a thin layer of scum on the surface of the liquid, and while of advantage in preventing further oxidation, offers also a great disadvantage in that the solution always contains some of this precipitate. The soluble ferric compounds produced by oxidation do not accumulate in any quantity, as in contact with the freshly deposited iron they are subsequently reduced, thus—



Vats containing ferrous compounds should therefore be kept air-tight when not in use. Care must, however, be taken that water for preparing the solutions is first boiled well. All ordinary waters, and even distilled waters, contain enough dissolved oxygen to start the oxidation of the iron compounds. By boiling, much of this gas is expelled and the iron compounds are therefore much more stable. Sulphuric acid would prevent the oxidation to a considerable extent, but this or any other mineral acid could not be permitted in a solution from which iron is to be deposited, as a considerable quantity of

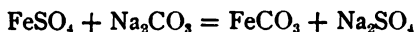
hydrogen would be evolved at the cathode with a proportionately smaller amount of iron, or even no deposition of iron at all.

Solutions.—

- (1) Ferrous ammonium sulphate 1 lb.
 Water 1 gallon.

This solution is similar in composition to the nickel bath, and is worked on practically the same lines. No free mineral acid can be present, and should it be formed by the inefficient solution of the anode, it must be neutralized either by ammonia or even by a small quantity of precipitated and washed ferrous carbonate (made by adding to ferrous sulphate solution a washing-soda solution). Acetic acid in small amount is allowable in the solution.

(2) Ferrous sulphate or iron protosulphate alone gives a good deposit. A good solution can be made by dissolving the commercial salt in water, and precipitating the carbonate with washing-soda solution—



The washing-soda solution is added until no further precipitate is formed. The precipitate is allowed to settle and the clear liquid poured away. The precipitate is now washed several times with clean water and is finally dissolved in dilute sulphuric acid, preferably made with boiled or distilled water. The precipitated iron carbonate readily dissolves in the acid, an excess of which must be avoided. If too much acid is accidentally added it can be neutralized by the addition of a further small quantity of precipitated ferrous carbonate.

(3) The electrolytic method has also been strongly recommended. It is carried out in the following manner. A strong solution (1–2 lbs. per gallon) of ammonium chloridé or sal-ammoniac is prepared, and through it a current of electricity is passed, using a plate of soft wrought iron as anode, with a cathode contained in a porous cell filled with the electrolyte.

A fairly high current density at the anode is used, and the anode dissolves freely under its influence, producing ferrous chloride (FeCl_2), which, with the excess of ammonium chloride, constitutes the electrolyte.

The Deposit.—The process of iron deposition has long been called **steel-facing**. This is a misnomer. Deposited metals are usually characterized by their purity, and iron is not a prominent exception. Now, steel is iron containing carbon in varying quantity from quite a small amount up to about $1\frac{1}{2}$ per cent. The carbon imparts considerable hardness to the iron. The hardness of the deposit of iron at first gave rise to the impression that it was steel, and hence the name “steel-facing.” Analysis of the deposit shows that it contains practically no carbon at all. The little which has sometimes been found is almost accidental, and is never equal in amount to that in the anode. The matter is one of importance. For carbon to be deposited, carbon must pass through the solution in the “ionic” form. Such a form of carbon is not known at present, and should it be discovered, some important applications may await it.

The deposit, however, though containing practically no carbon, does contain one impurity sometimes in appreciable amount. This is hydrogen, which is deposited with the iron and absorbed or “occluded” by it. In one case a sample of electro-deposited iron was found to contain as much as 240 times its volume of hydrogen, and, although by weight this would appear to be a much smaller amount—about 0.27 per cent.—it considerably influences its properties, producing a metal which is hard and brittle. Further, this hydrogen may be lost by heating, and annealing restores the original properties of iron, though the change is attributed by some to other causes.

Anodes should be of best wrought iron. Swedish charcoal iron is to be preferred, containing little carbon, few other impurities, and those only in very small amounts. It dissolves readily under electrolytic corrosion. Mild steel and harder

steels are but slowly dissolved, and this induces acidity in the solution, which is to be avoided. The anodes should be first pickled and scoured by the methods described on p. 132 to remove the coating of oxide usually present. As the iron dissolves in the bath, so a thin film of carbon appears on the anode. The anodes should then be removed from the vat and scoured. The black deposit is readily removed, leaving the clean surface of the metal exposed. Anodes may be suspended by iron hooks, and when the bath is not in use should be lowered below the surface of the liquid to protect them from considerable oxidation and corrosion.

Current Conditions.—The allowable current density is controlled chiefly by the strength of the solution. A high C.D. will produce gas which gives rise to burning, but this is less likely when the solution is strong. A strong solution with a low current density is therefore to be aimed at. From most solutions the deposit is of a light grey to steel colour, and thicker deposits are brittle until annealed. For "steel-facing" engraved plates, from five to ten minutes' deposition is sufficient. Thicker deposits would produce a blurred impression. With an excessive current the deposit darkens upon the edges, and may peel off in the form of small spangles.

The Process of Deposition.—Much the same precautions are required for iron as for nickel, and the same care must be exercised in cleaning work preparatory to deposition. The deposition of iron is confined almost entirely to the coating of engraved copper-plates, and in any case these can only be put under very gentle treatment, otherwise the impression would be injured. Hot potash must first be applied to remove grease, using only a soft potash mop for this purpose. After thoroughly rinsing, the plate may next be passed through a weak sulphuric acid (1-20) and again rinsed. After a final dip through a weak cyanide, followed by thorough washing, the plate is put into the vat and supported by suitable clips so that no wire marks will be made. A momentary higher current density at first is an advantage, following nickel

practice, and, when completely covered, the current density is reduced for the remainder of the process. The plate should be examined when first covered, and if any dirt or scum from the solution is attached to it, this must be removed by scouring with a soft bristle brush under clean water. It is the final surface that counts, and every precaution must be taken to ensure that a satisfactory surface is maintained. After five to ten minutes' deposition the plate is removed, and most thoroughly rinsed in cold and hot water. The deposit is somewhat liable to retain small amounts of the liquid, and, being so susceptible to oxidation, unless this is entirely removed, a rapid oxidation and consequent deterioration of the plate will set in. After drying, it should be thinly coated with oil and the excess wiped off before being stored, or while it stands awaiting use.

Removal of Worn Deposit.—This can be effected with the greatest ease, and, when a plate is in use, needs to be done frequently. Iron dissolves readily in a weak sulphuric acid; but the rate of solution is promoted by its contact with the less positive copper. The plate is first cleaned from ink and grease, and placed in a shallow dish containing sulphuric acid of not more than 10 per cent. strength. From any points where the copper shows through, the rate at which iron dissolves is considerable, and the bare patches soon grow in size, till in a short time the whole of the deposit has disappeared. The acid has absolutely no action on the copper, and the method is therefore quite safe. When the deposit has been removed, the plate only needs thorough rinsing and perhaps a light scouring with a soft bristle brush, and it may at once be transferred to the iron bath to receive a fresh deposit.

Deposition of Tin.

The deposition of this metal is practised on only a limited scale. The metal tin, on account of its whiteness and non-liability to tarnish, has long been used as a means of protecting iron and steel. For this purpose the tin is melted, and, at a

temperature not much above its melting-point, the previously cleaned iron or steel is passed through the metal and allowed to drain. A beautifully white and smooth coating is obtained, and tinplate is simply sheet iron or steel which has been tinned by this method. In many cases, however, owing to the high price of tin, lead is added, producing a less expensive but distinctly inferior alloy. By this simple "dry" process substantial coatings are put on, and the metal is used for numerous purposes.

Simple Immersion.—For small articles a solution method is used, and a large amount of small work, such as pins, hooks, eyes, etc., is treated in this manner. The solution consists of a mixture of a tin compound with some solvent for it. Stannous chloride or tin protochloride (SnCl_2) is invariably used, and this is added as required to a strong solution of cream of tartar (potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$). The action is facilitated by the presence of tin, either in the grain or sheet form. Alternate layers of small articles with sheets of tin may be used, and in a short time the brass articles become nicely whitened with tin, and may be rinsed and dried off and a little further polish imparted by shaking in a barrel.

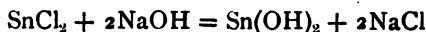
Single Cell Methods.—A slight modification of the method enables thicker deposits to be made. If in the solution previously described the articles are in contact with zinc, the tin is deposited at the expense of the zinc. This may be accomplished by using granulated zinc thrown amongst the articles in the solution, or, better still, by supporting the small work in shallow trays improvised from zinc sheet. It will be apparent that no tin is being added to the solution while the tinning is going on, and frequent additions of tin protochloride will be required and the solution rejected when much zinc has accumulated in it. By this or similar methods—and many variations may be worked upon it—thicker deposits can be obtained than by the ordinary simple immersion process.

Electrolytic Method.—A number of tin compounds

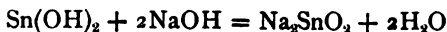
may be used with quite satisfactory results. Stannous chloride, however, is not numbered among them. From this solution tin may be deposited in the form of beautiful long shining crystals, interesting in a way, but not at all suitable for the purposes now under consideration.

Solution I.—Roseleur recommends the following method: A solution of sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) is made by dissolving 1 lb. of the salt in 10 gallons of water. To this solution is added from 1 to 2 ozs. of tin protochloride. This may conveniently be dissolved in water first, and on adding to the pyrophosphate solution a milkiness and precipitate is first formed, which dissolves on stirring. The clear solution is then ready for use.

Solution II.—Another good solution can be made from stannous chloride by the addition of an excess of caustic soda or potash. The first addition produces a precipitate of stannous hydrate, $\text{Sn}(\text{OH})_2$.



The precipitate dissolves in an excess of the alkali, forming sodium stannite (Na_2SnO_2), which is soluble.



It is probable that the tin is deposited as the result of a secondary reaction. Such solutions may be made of any strength, and from the strong solutions it is possible to obtain the tin quantitatively—that is, in amount in accordance with Faraday's law, by attention to the few essential conditions. In this solution also the anodes are quantitatively corroded, and little or no variation in the strength of the solution occurs, though any deficiency can be readily made good by the addition of more stannous chloride, so long as an excess of alkali is already present.

Solution III.—A similar solution may be prepared from the metal as follows:—

Granulated tin is first treated with nitric acid (1-1), until

it is completely converted into a white insoluble powder, which is practically a hydrated oxide of tin. Excess of acid is evaporated off or got rid of by repeated washing with water. The washed precipitate is then treated with a strong solution of caustic soda in which it is soluble, the solution being facilitated by warming. Any small insoluble portion may be neglected. The solution contains sodium stannate (Na_2SnO_3), and may be diluted at will. Here again the deposited tin is probably a secondary product of electrolysis.

Solution IV.—Good deposits can also be obtained from a solution prepared from stannous chloride and ammonium oxalate. To prepare 2 litres (= nearly half a gallon), dissolve 60 grams of crystallized stannous chloride in about 800 c.c. of water. The solution is not clear, the turbidity often occurring with tin salts. Dissolve 125 grams of ammonium oxalate and 5 grams of oxalic acid in 800 c.c. of water. This may require warming. The oxalate solution is now added to the tin solution, with shaking. A white precipitate is first formed, which redissolves when the whole of the oxalate solution is added. The solution is now diluted till its volume is 2 litres, and may be even further diluted. The solution contains a double oxalate of tin and ammonium, and yields excellent deposits. With the solution prepared as above, quantitative results can be obtained with ease if warming and stirring are effected, and the corrosion of the anode proceeds quite normally, there being thus little need for the frequent or even only occasional additions of tin compounds. This solution has the advantage that it can be freely mixed with a similarly prepared solution of copper, and from the mixture in suitable proportions the mixed metals—the alloy bronze—can be deposited (see p. 252). Other tin and copper solutions are not so easily and freely mixed.

Many other solutions for the deposition of tin with the separate current have been described and patented, details of which can be easily referred to should necessity arise. The demand for electro-deposited tin is, however, so small that,

with one or other of the solutions described above, all ordinary requirements can be satisfactorily met.

Anodes should be of pure tin. This may be obtained in the form of sheet or cast metal. At nearly £150 per ton a heavy cast anode is a considerable item. The sheet metal serves the purpose admirably, and is, comparatively speaking, not so much harder than the cast metal to considerably affect its rate of corrosion. Tin-plate—that is, iron covered with tin by the “dry” process—is not suitable for anodes. The tin it possesses will, of course, be dissolved, after which the anode becomes insoluble. As a matter of fact, scrap tinned iron contains about 5 per cent. of its weight of tin, and the problem of obtaining this tin by making the scrap an anode in a suitable solution has proved an attractive one to electro-metallurgists, especially in view of the enormous amount of scrap produced. Many methods have been devised to treat this material. In some processes the scrap is made the anode in a suitable solution into which it dissolves and is subsequently deposited. In other methods the tin is dissolved by chemical means and subsequently obtained by electrolysis. The problem is an interesting one from both the purely scientific and commercial standpoints. Reverting, however, to the subject of tin anodes, care must be taken not to use some of the commoner brands of tin which may contain considerable amounts of the cheaper metal, lead. Such alloys are duller than the pure tin. They dissolve well as anodes, but lead finds its way into the liquid and soon becomes deposited.

Character of Deposit.—The tin obtained from these solutions is, within certain limits of current density, white and dull. It is improved considerably by scratch-brushing, though on account of the softness of the deposit only a very light brushing is required. With a heavy type of brush the deposit would soon be worn through. Beyond the somewhat narrow limits of this dull white deposit the usual burning occurs, though in a much more pronounced degree than with

many metals, the deposit soon assuming a dark grey and powdery character. In any quantity the tin is of a soft spongy nature, and can be easily wiped off with the finger and compressed. It has long been known that the addition of quite small quantities of some substances in a plating solution considerably improves the character of the deposit. This is most pronounced in the case of tin by the addition of glue or gelatine to the very limited extent of 1 gram per litre. This slight addition to the bath serves to completely alter the character of the deposited tin. Without it, a given current may produce a spongy and dark deposit. Without making any change in the conditions, except this slight addition, the deposit is changed to a white and coherent mass, which stands scratch-brushing without any signs of stripping. The safe limits of current density are thus considerably widened. The effect is lost after a time, and small additions of gelatine need to be made. This remarkable effect has been applied in other prominent cases of electro-deposition, though the "why and wherefore" of the beneficial effect is not so easily answered.

Deposition of Zinc.

As the deposition of zinc is so little practised apart from its application in electro-brassing (Chapter XVIII.), it calls for but little comment.

From the cyanide solution prepared on similar lines to those for the cyanide copper, zinc is obtained in a good adherent form, and thick deposits can be obtained with ease.

If any attempt is made to obtain zinc from the sulphate solution, it will be necessary to ensure that the solution does not become acid even to a most limited extent. Slight acidity is possible with nickel, undesirable with iron, and absolutely fatal with zinc. A neutral solution of zinc sulphate readily yields a deposit of the metal, but as the anode may not corrode to an extent equal to the deposition of the metal,

acidity soon occurs. Yet the sulphate is desirable on account of its cheapness, while on any considerable scale the cyanide solution is costly. Cowper-Coles surmounts the difficulty by using the sulphate solution with an insoluble anode of lead. The acid formed is neutralized, and at the same time the zinc content of the solution maintained, by circulating the liquid through the vat and also through filter-beds of zinc dust. Zinc dust is a by-product of the zinc extraction process, and contains the metal in a powdered form with oxide. It can be obtained at a comparatively low cost, and is quickly absorbed by the faintly acid solution. The method is very effective, and allows of the use of the sulphate solution for the deposition of zinc on the large scale for covering plates, tubes, and other heavy iron work.

Zinc is, of course, very largely applied to iron work by the "dry" process of galvanizing, in which the cleansed metal is passed through a bath of molten zinc. One of the disadvantages of this method, however, is the temperature to which all the work must be raised in passing through the bath of molten metal, and also the irregular draining of the excess of zinc from parts which have to be subsequently fitted together. Electro-galvanizing quite obviates these difficulties, and more recently Cowper-Coles has perfected a process to which the name "sherardizing" has been given. In this process the articles to be galvanized are cleaned and imbedded in zinc dust in suitable boxes, which are then closed and heated in a furnace to about 300° C. The zinc dust attaches itself to the metal in a very uniform manner, the thickness of the deposit being dependent upon the temperature and duration of heating. The "sherardized" articles have a dull colour.

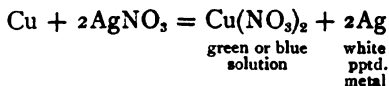
Many other preparations have been suggested for electro-zincing, but none are used on any considerable scale. From many of them zinc is obtained in a perfectly reguline form, but it is to be observed that high current densities are to be preferred. Of the two elements, hydrogen and zinc, the former

is far more easily deposited, and while it can and does turn out copper from the sulphate solution, as in the Daniell cell, it is quite incapable of similarly precipitating zinc. Conditions for successful zinc deposition must therefore be those which are not favourable to hydrogen deposition, and higher current densities therefore give less gas, and the absence of any constituent which produces hydrogen ions in considerable quantity is also necessary.

CHAPTER XVI

Deposition of Silver

Introduction.—The position of silver in the electro-chemical series is at once an indication that its salts are capable of easy decomposition, and electro-deposition of the metal is consequently readily effected. For example, copper placed in silver nitrate dissolves, precipitating the metal silver thus—



Obviously, therefore, special precautions will be necessary to prevent this unsatisfactory simple immersion deposition in the plating process. Again, most salts of silver are decomposed by heating, the metal usually remaining. This easy decomposition of silver compounds also means a difficulty in forming them. As a result, silver is not readily oxidized. Oxygen, dry or moist, has no action on the metal. It does not rust. Sulphuretted hydrogen, however, tarnishes it rapidly. The metal is not easily corroded by the acids which ordinarily occur in food stuffs, hence the extensive use of silver-plated goods for table use.

The metal is soft, very white, easily burnished, and is capable of taking a fine polish. Pleasing effects may also be produced upon it by chemical means. From most points of view, therefore, silver is a metal much to be desired for coating baser metals, both for utility and ornamentation.

Materials available.—While many silver compounds may be obtained, only a few find application for plating

purposes, and for the greater part these may be best prepared from the metal. For this purpose the metal should be "fine," that is, pure. Ordinary sterling silver contains $7\frac{1}{2}$ per cent. of copper. The use of such a metal would introduce and concentrate copper in the silver bath. This is not desirable. Fine silver only should be used. For solution purposes it may be bought as grain silver at about two shillings an ounce (troy).

Silver nitrate (AgNO_3) can be bought in a crystalline form, suitable for most purposes, at about 2s. od. per oz. The formula (AgNO_3) shows that it contains only $\frac{108}{108 + 14 + 48} = \frac{108}{170}$, or 63.6 per cent. of its weight of silver. A comparison of the cost of silver and its nitrate may thus be made. Suppose we wish to make up 100 gallons of solution containing 2 ozs. metal per gallon. We require 200 ozs. metal. Bought as metal the cost is—

$$200 \times 2s. \text{ od. (say)} = \text{£}20$$

As nitrate we should need to buy—

170 ozs. to obtain 108 ozs. metal.

$\frac{170}{108}$ " " 1 " "

$\frac{170}{108} \times \frac{200}{1}$ ozs. " 200 " "

$$= 315 \text{ ozs.}$$

$$315 \text{ ozs. at } 2s. \text{ od.} = \text{£}31 \text{ } 10s. \text{ od.,}$$

approximately, £10 more than in the case of the metal. Against this £10 saving by buying the metal, we should have to set the cost of the acid required, and the time and trouble and small loss in the process of dissolving the metal. A £10 margin is an ample allowance with which to do this, granting ordinary conveniences. The cyanides of silver, single cyanide (AgCN), and double cyanide (AgCN.KCN) are procurable,

but their ease of preparation is such as would not warrant their purchase.

Simple Immersion Methods.—Solutions for depositing silver by simple immersion are most numerous, and of greatly differing composition. Besides the silver compound, which may be chloride or cyanide, a material is required which will take it into solution, and a choice may be made between potassium cyanide, cream of tartar, sodium chloride, etc.

A simple solution may be made as follows :—

	Parts by weight.
Silver chloride (AgCl)	1
Potassium bitartrate ($\text{K.HC}_4\text{H}_4\text{O}_6$)	50
Sodium chloride (NaCl)	50

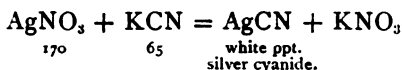
Potassium bitartrate and salt are mixed in equal quantities, and silver chloride added in small quantity. The mixture may be ground to a paste with a little water, and poured a little at a time into boiling water. The articles to be silvered should be cleaned by the usual dipping processes, and introduced into the hot silver solution. They quickly receive a deposit of silver, the rate of deposition depending upon the amount of silver in the solution. The deposit of silver, however, is very slight, and cannot be thickened. As silver is taken from the solution, so more of the paste should be added. An older solution works somewhat better than a new one, and in course of time the solution acquires a considerable amount of copper, which, however, need not interfere with the silver deposition, unless zinc articles are present among the work. On account of the thinness of the deposit the process is termed "whitening." It will be seen also that by using the paste without addition of more water, silver can be deposited on metal surfaces by merely rubbing the work with a damp rag occasionally dipped in the paste. For large flat surfaces this is more convenient than immersion in a solution. After the surface is satisfactorily whitened, it may be rinsed through first cold and then hot water, and dried off in sawdust.

Preparation of Electro-silvering Solution.—For the deposition of silver by means of the electric current, a simple and most satisfactory solution can be made up. The essential constituent is double cyanide of silver and potassium (AgCN.KCN), which may be prepared from the metal or the nitrate. The following equations show clearly the quantities of materials required :—

Silver nitrate (AgNO_3) contains—

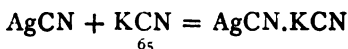
$$\text{AgNO}_3 = \frac{108}{108 + 14 + 48} = \frac{108}{170} = 0.636 \text{ of its weight of silver.}$$

On adding cyanide to silver nitrate—

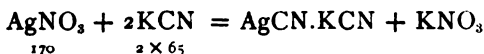


the single cyanide of silver is precipitated. It requires 65 parts by weight of potassium cyanide to convert 170 parts by weight of nitrate into single cyanide.

Further—



The single cyanide thus formed requires a further 65 parts by weight of potassium cyanide to convert it into the soluble double cyanide. Or we may write—



which states that 130 parts of potassium cyanide are required to convert 170 parts by weight of nitrate into double cyanide. Now, the silver-plating solution may contain 1, 2, 3, or 4 ozs. of metal per gallon. In this case take 2 ozs. of metal per gallon.

100 gallons would require 200 ozs. of metal.

Now, $108 \text{ Ag yield } 170 \text{ AgNO}_3$
 $\therefore 200 \text{ ozs. Ag yield } 315 \text{ ozs. AgNO}_3$

For conversion with single cyanide—

$$\begin{aligned}
 &170 \text{ AgNO}_3 \text{ require } 65 \text{ KCN} \\
 \therefore 315 \text{ ozs. } & \text{,,} \quad \text{,,} \quad \frac{65 \times 315}{170} \text{ ozs. KCN} \\
 &= 120 \text{ ozs.}
 \end{aligned}$$

A similar amount will then dissolve the single cyanide, and when this is done, a further supply of 120 ozs. of cyanide may be added for "free cyanide," making a total of 360 ozs. of cyanide. These, however, are troy ounces, and should therefore be converted into ounces avoirdupois.

$$\begin{aligned}
 &\text{Now, } 1 \text{ oz. troy} = 480 \text{ grains} \\
 &\text{and } 1 \text{ oz. av.} = 437.5 \text{ grains} \\
 \therefore 1 \text{ oz. troy} &= \frac{480}{437.5} \text{ ozs. av.} = 1.1 \text{ ozs. av.} \\
 \text{and } 360 \text{ oz. troy} &= 360 \times 1.1 = 396 \text{ ozs. av.} \\
 &= \frac{396}{16} = 25 \text{ lbs. about.}
 \end{aligned}$$

For ordinary purposes we may say 2 ozs. troy of metal, or 3.15 ozs. troy of the nitrate, and 4 ozs. av. of cyanide per gallon.

The materials are worked up as follows :—

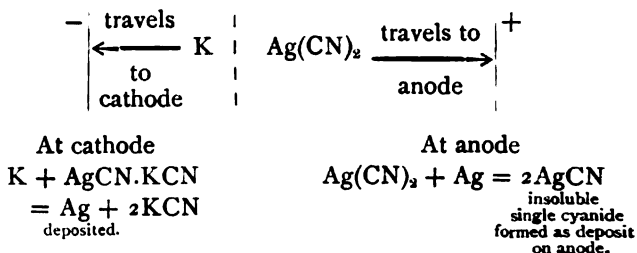
Using the nitrate, dissolve this in a quart or more of distilled water. Dissolve the cyanide in a similar volume of water. Add the cyanide solution to the nitrate solution a little at a time, with constant shaking, allowing to settle after each addition and shaking. The precipitated cyanide readily settles, and leaves a fairly clear liquid. The cyanide should be added until no further precipitate is formed. It will require about one-third of the cyanide, and as this amount is approached the cyanide should be added most carefully. The precipitation is complete when a further addition of cyanide produces no turbidity. Allow to thoroughly settle, and carefully pour off the clear liquid. As this liquid may contain a little silver, due to a slight excess of KCN being added, it should be reserved for the recovery of

any silver it may contain. The precipitate is now covered with tap-water, well shaken, allowed to settle, and the water poured away. This should be done again, leaving the washed precipitate undisturbed. More cyanide solution is now added to the precipitate, with shaking, until it is completely dissolved. This should require about one-half of the cyanide remaining from the first operation. During the process a darkening occurs, due to impurities which can only be avoided in the very best materials. The remainder of the cyanide solution can now be added, and the solution made up to 1 gallon with distilled water. On allowing to settle, only a faint trace of dark precipitate remains, and this is usually so small that it may be neglected. The specific gravity of such a solution is 1.025 (4° B. or 5° Tw.).

Conversion of Metal into Nitrate.—The granulated metal or sheet is covered with distilled water and pure nitric acid added in about equal volume. This may be done in glass, porcelain, or earthenware vessels, preferably flat and open ones, and such as can be heated by means of a water-bath. On warming, a violent action sets in, and brown fumes are evolved. If an excess of acid is used, the metal completely dissolves. If insufficient acid has been added, then some silver remains undissolved, in which case pour off the clear liquid into another vessel and slowly evaporate it. The undissolved silver may now be attacked with more acid, and afterwards evaporated either with or apart from the first solution. When the solution is evaporated down to saturation, crystals begin to form on the surface. On cooling the solution a large amount of the nitrate is obtained as crystals. Pour off the clear liquid, wash the crystals with a little distilled water once—adding the washing water to the solution. Evaporate the solution further, and obtain another crop of crystals. Treat as before, and finally evaporate the solution to dryness, avoiding overheating, which blackens the nitrate by decomposition. The whole of the nitrate—crystals and final residue—is now dissolved in distilled water, and is ready for precipitation with cyanide.

Other Solutions.—Numerous other methods have been suggested for preparing silver-plating solutions. Thus the silver nitrate may be “thrown down” (as AgCl) by common salt solution, after which the precipitate is dissolved in cyanide. Such a solution produces a dead-white deposit. Again, the bath may be prepared electrolytically by making a sheet of silver the anode in a cyanide solution (4 ozs. per gallon). For the cathode, any metal plate in a porous pot containing some of the cyanide will serve. As a current is passed the silver dissolves from the plate, and cannot be deposited on the cathode. The amount which has passed into solution can easily be arrived at by weighing, and as silver may pass to some extent through the porous cell, the solution in the cell should be occasionally replaced by fresh cyanide solution.

The Necessity of Free Cyanide.—When a silver-plating solution is electrolyzed, the action which occurs may be represented thus—



Then without free cyanide the anode would soon become covered with a deposit of silver cyanide, which, on account of its resistance, considerably reduces the current—even down to zero. To keep the anode clean more cyanide is necessary. This is being formed in just the right amount at the cathode, but it is required at the anode. As it diffuses only slowly it is necessary to keep in the solution a certain excess of cyanide called “free cyanide.” Sufficient is required to keep the anodes clean and prevent the falling off of the current. With too much free KCN, the anodes work very white, dissolve

away too rapidly, and, in addition to this, the solution more readily gives up silver by simple immersion. This is a disadvantage.

Test for Free KCN.—A small quantity of the plating solution is taken in a test tube or test glass, and a solution of silver nitrate is added a drop at a time. Free cyanide is shown by the fact that no precipitate is formed, or if a precipitate is formed, it immediately redissolves. In the absence of free cyanide, a precipitate is formed which is not soluble on stirring or shaking. A relative idea of the amount of free cyanide present may be gathered from the quantity of the silver nitrate solution required to produce a permanent precipitate, and a method for exact determination based on this principle is described in Chapter XXIII. The behaviour of a solution without and with free cyanide may be seen from the following figures from an actual experiment. In each case the anode and cathode were of the same area and distance apart.

TABLE XIX.

EFFECT OF FREE KCN IN SILVER BATH.

Solution.	P.D. Volts. (V).	Current Amperes (C).	$\frac{V}{C} = R$ (ohms).
No free KCN.	2.45	0.8	3.06
1st addition of KCN . .	0.5	2	0.25
2nd addition of KCN . .	0.34	2	0.17

Anodes.—Efficient anode solution is an essential for maintaining the solution of uniform composition as regards its content of metal. Anodes are usually obtainable in the form of pure sheet. The rolled metal is hard and not easily dissolved. Annealing makes it much more susceptible to solution. For this purpose anodes might be heated to redness (say, about 800° C.) in a muffle or on a charcoal fire and allowed to cool slowly.

As a matter of economy it is desirable to place the anode as completely as possible in the solution. For this purpose it may be supported with silver or platinum wire either soldered or preferably welded to the plate. If soldered, the joint should be kept out of the solution, as it will be liable to more rapid corrosion than the silver. Another method is to cut the anode, as shown by dotted lines in Fig. 105, forming two strips which can then be bent in the form of hooks for suspending on the anode rods.

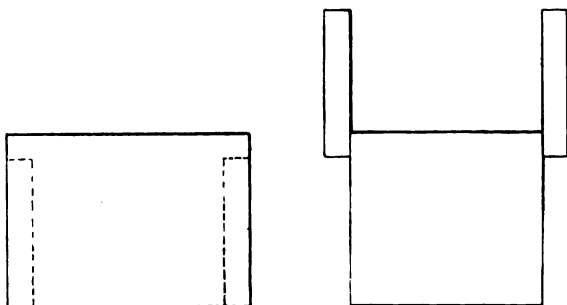


FIG. 105.—Silver anode.

Vats.—On the small scale, enamelled iron tanks are very convenient; outside the range of these, however, lead-lined wooden vats are suitable, though not so clean as those of enamelled iron. In any case, it is very desirable that a well-fitting cover should be provided to keep out dust when the bath is not in use.

E.M.F. and C.D. required.—It has been pointed out previously that these values are very variable and depend upon a number of conditions. Taking the current density for a solution containing 2 ozs. metal per gallon, the following results were obtained in a small vat.

Two anodes and a cathode, each of 8 square inches, were placed 1 inch apart—one cathode between two anodes. The current was varied by external resistance.

TABLE XX.

EFFECT OF CURRENT DENSITY IN THE SILVER BATH.

Experiment.	C (amperes).	C.D.	P.D. (volts).	Remarks.
1	0.20	3.6	0.8	Fine granular deposit.
2	0.40	7.2	1.4	Granular deposit.
3	0.60	10.8	1.7	Edges slightly burnt.
4	0.80	14.4	2.0	Edges badly burnt.

It will thus be seen that for these conditions a C.D. of 10 must not be exceeded, this being obtained by a P.D. of less than 2 volts. In the case of irregular work the distance of anode and cathode is necessarily greater, requiring a higher P.D. to maintain the same C.D. With more free KCN the P.D. would be reduced; with a weaker solution a lower limit of C.D. must be set. The figures, in any case, are variable, and should be determined for each particular case and subsequently adhered to.

Character of Deposit.—Silver deposits are for the most part dull white, but even under this general description there may be a wide variation. Thus low C.D.'s produce a minutely crystalline deposit readily distinguishable under a low-power microscope. The deposit is of good quality and very coherent. High C.D.'s produce deposits which become flaky or powdery and grey. This is due to the evolution of hydrogen, but between these extremes there is a wide mean through which perfectly white and granular deposits are obtained. It will be remembered that silver is deposited at over three times the rate of copper, and on this account also the C.D. must be kept low. With the same current the weight of silver to that of copper (from sulphate) is as 3.42 : 1, while, with the same C.D., the thickness of Ag to copper is as 2.9 : 1.

Preparation of Work.—The deposition of silver does not present any serious difficulty, but a number of operations preliminary to deposition are essential. Of the common metals,

copper, brass, and German silver are most easily plated. It is first necessary to thoroughly clean the work by the usual processes following polishing. It will then be observed that in some plating solutions, especially those containing an excess of free cyanide, a slight coating of silver occurs by simple immersion. Now, simple immersion deposits are not noted for adherence, and still less so are thicker deposits placed upon them. To avoid this simple immersion, recourse is had to—

Quicking.—This term denotes a further preliminary operation of passing the prepared work through a solution of mercury cyanide. Mercury is less positive than either copper or silver. In such a solution, copper, brass, and German silver receive a bright deposit of mercury, and when thus covered the work is thoroughly rinsed and transferred to the silver bath, when, on account of mercury being less positive than silver, no deposition of silver by simple immersion can occur, and the subsequent electrolytic deposit is more adherent.

Advantages of Quicking.—(1) The mercury deposit is less liable to tarnish than the work, and a cleaner surface is therefore presented to receive the deposit of silver.

(2) Deposition of silver by simple immersion is prevented.

(3) Possibly amalgamation and greater adhesion of the deposit and work occurs.

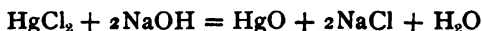
Quicking Solution.—This may be made to contain about 1 oz. of metal per gallon. The metal, which dissolves in nitric acid, or the nitrate or chloride may be used.

Hg	Hg(NO ₃) ₂ ·8H ₂ O	HgCl ₂
200	200 + (2 × 62) + (8 × 18)	200 + 71
200	468	271

or as

1 OZ. : 2·34 OZS. : 1·35 OZS.

The nitrate or chloride is dissolved in water and caustic soda solution added until there is no further precipitate. The precipitate is practically mercuric oxide—



It is allowed to settle, and the clear liquid poured away. After washing the precipitate with water it is dissolved in a quart of cyanide solution containing 4 ozs. cyanide. A slight black precipitate remains. Neglecting this, the clear solution may be poured off and made up to 1 gallon.

Deposition of Silver on Brass, Copper, and German Silver.—After the preliminary polishing, the work is well scoured with potash and subsequently with fine pumice powder. This produces a finely dull but uniform surface. After rinsing, it is passed through the “quicking” solution, from which it should receive a bright deposit of mercury, and after further rinsing should be transferred to the bath. It should be instantly coated with silver and the current adjusted to give a finely granular deposit. If the deposit is not uniform, recourse may be had to scratch-brushing, or where the defective portion is in an awkward position or in the case where scratch-brushing cannot be safely applied, it may be rubbed with pumice powder by means of a piece of wood covered with cloth. After rinsing, the work is replaced in the bath. There should be no sign of darkness about the deposit. Slinging wires should be shifted occasionally to avoid marking the work, and deep work should be inverted occasionally during the deposition, as there is a tendency to the production of thicker deposits at the bottom than at the top of the solution. Anode surface should be large and spaced equally from the different pieces of the work. More prominent portions of the work are apt to collect a larger share of the current, and hence receive a somewhat thicker deposit. This is an advantage, as these portions receive the greater wear in subsequent polishing and use.

Deposition on Other Metals.—Zinc and iron should first receive a deposit of copper from the cyanide solution, and subsequently treated as copper.

Britannia metal, pewter, and lead alloys generally, may be first coppered and then quicked, but common practice follows another method called—

Striking.—This consists of avoiding the preliminary

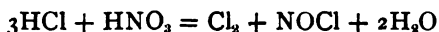
coppering in the cases of Britannia metal and the lead alloys generally, by introducing the clean work straight into a silver-plating bath, and using a somewhat greater current density than usual to ensure a rapid deposit. A separate solution is kept for this purpose, and after this first coating the work is transferred to the main bath to receive the bulk of the deposit. This preliminary deposit also achieves another purpose. Lead and lead alloys do not conduct so well as copper and brass. Of lead and copper work hanging from a cathode bar, the latter will more quickly be covered and receive a greater share of the current. The preliminary striking of lead alloys, therefore, removes this disadvantage. Moreover, metals of different character hanging from the same bar may give rise to a kind of local action, the more positive metal being corroded. This is a possibility to be avoided.

Bright Plating.—The usual silver deposit is dull. In 1847 it was observed by Milward that the addition of a little carbon disulphide (CS_2) to the bath results in a bright deposit which obviates the necessity of much subsequent burnishing and polishing. It is a remarkable result, attained by a surprisingly small amount of the substance—not more than 2 grains per gallon. In following this method it is usual to take a portion of the bath in a bottle, and add to it carbon disulphide in the proportion of 6 ozs. per gallon. This, on shaking well, forms a stock solution from which small quantities may be added to the main solution at the rate of 1 oz. per day in 10 gallons. Further, while the result is obtained with this small amount, a distinctly larger amount fails to produce the same effect. A satisfactory explanation of the phenomenon is not forthcoming. The deposit contains a trace of sulphur, too small, it would seem, to account for so considerable a change.

CHAPTER XVII

Deposition of Gold

Gold.—This metal is, from the plater's point of view, chiefly remarkable for its permanence in air, suffering only the faintest tarnishing with very long exposure, and even then being very easily cleaned. It is unaffected by oxygen, either at low or high temperatures. None of the ordinary acids singly act upon it. It is, therefore, usually dissolved in a warm mixture of nitric and hydrochloric acids called *aqua regia*, when—



The metal is attacked by the chlorine liberated, forming gold chloride (AuCl_3). As gold is not dissolved by nitric acid, this acid can be used to separate silver from its alloy with gold.

Gold is also dissolved, though only slowly, by a solution of potassium cyanide in contact with air. This fact is applied in the "cyanide" method of extracting gold from auriferous quartz. For a like reason, a gold anode should not be allowed to remain in the gilding solution when not in use, as it may be cut through at the "water" line. A disadvantage of the metal for covering baser metals is its softness, on which account also it is hardened by alloying with copper, the English gold coin consisting of 91.66 parts of gold and 8.34 parts by weight of copper. In order to diminish the cost of the metal, to enhance its colour and increase its hardness, it is alloyed with copper, the composition of the alloys being expressed in "carats." Thus pure or fine gold represents 24 carats. Other common alloys are shown in Table XXI.

TABLE XXI.

COMPOSITION OF GOLD ALLOYS.

Carat.	Percentage of gold.	Carat.	Percentage of gold.
24	100·0	15	62·5
22	91·66	12	50·0
18	75·0	9	37·5

Standard or coinage gold is thus 22 carat. The alloy becomes redder with increasing amounts of copper, the presence of which, in appreciable quantity, can easily be detected by the application of a drop of strong nitric acid, which attacks the copper and leaves a yellow stain.

Compounds of Gold.—The compounds of gold available for preparing gilding solutions are comparatively few, and are usually prepared from the metal.

Chloride of Gold (AuCl_3) is a yellow deliquescent crystalline compound, made by dissolving the metal in *aqua regia* and evaporating down to dryness. Its formation is invariably the first stage in the production of other gold compounds. In preparing it, fine gold should be placed in a small flask, or preferably a bulb of the shape shown in Fig. 106, covered with water, and the mixed nitric and hydrochloric acids added a little at a time. A vigorous action soon sets in. More acid can be added when effervescence ceases, until the gold entirely disappears. The heating is effected most safely by standing the bulb in a beaker or saucepan of water, which can be conveniently heated. When the metal is completely dissolved, the liquid is evaporated to dryness in a porcelain dish, standing over boiling water. Overheating brings about the decomposition of the chloride, the salt being very unstable.



FIG. 106.—Bulb for dissolving gold.

After evaporating just to dryness, it should be dissolved in distilled water, and is best kept in this form till ready for use.

With this solution, ammonia gives a reddish-yellow precipitate of "**fulminate of gold.**" It is exceedingly explosive when dry, and, if prepared, should most carefully be kept damp. The precipitate is soluble in potassium cyanide, forming the **double cyanide of gold and potassium.** Ferrous sulphate solution readily throws down the gold from the chloride and other gold solutions, thus—



and this reaction is used in the recovery of gold.

Sulphuretted hydrogen precipitates the two **sulphides of gold** (1) auric sulphide (Au_2S_3) from a cold solution; and (2) aurous sulphide (Au_2S) from a hot solution.

Gilding.—Gold is an electro-negative metal. It forms compounds which are not very stable, and are therefore readily decomposed. The metal is easily deposited by simple immersion. In general, the methods of applying gold to metallic surfaces are—

- (1) By means of mercury, as in mercurial gilding.
- (2) Simple immersion methods.
- (3) Electro-deposition by means of the current.

Mercury Gilding was considerably practised at one time, previous to the wider introduction of the electro method, and is still in use for some classes of work. The gold is applied to the metallic surface in the form of an amalgam (an alloy with mercury). Mercury dissolves most metals, and gold is not an exception. The resulting amalgam made by pouring mercury on to hot gold may be rid of a large excess of mercury by squeezing it through chamois leather, the residue being pasty, and is kept in this condition under water. This amalgam is applied to the clean surface by means of a wire brush, first dipped in nitrate of mercury and afterwards passed over the amalgam, and finally rubbed on the work, the operation being repeated until a uniform result of

sufficient thickness has been obtained. It is then rinsed and dried. The mercury is now expelled by slowly raising the temperature on a dull charcoal fire. Mercury volatilizes at 390° C., and is thus easily expelled. The article is then scratch-brushed, reheated, and scratch-brushed again, when the characteristic pale yellow colour of gold is acquired. The pale colour not being much in demand, is improved upon by dipping the work in a mixture of alum, nitre, and salt, made to a paste with water, and again holding the work over the fire till the mixture which is retained by the work just fuses. It is then plunged into water, which dissolves off the "colouring" materials.

Gilding by Simple Immersion.—This is possible on account of the very electro-negative character of gold, and the process has been most freely applied for the cheaper classes of work. The chief constituent of the solution is gold chloride. The following solution gives good results :—

	Parts by weight.
Gold chloride	10
Sodium pyrophosphate	80
Hydrocyanic acid	1
Water	1000

The amount of gold chloride may be considerably varied, the action being slower when little gold is present. The solution is used hot, and will require frequent small additions of both gold chloride and hydrocyanic acid. The work, suitably cleaned, should first receive a bright coat of mercury, either from the ordinary quickening solution, or from a weak solution of mercuric nitrate. The subsequent gold deposit is very thin, and may only be thickened to a limited extent by alternately quickening and passing to the gold bath after rinsing. Many other solutions may be prepared and used with effect. For these the student is referred to larger treatises.

Electro-gilding refers to the deposition of gold by means of the electric current. By this method the gold

deposit can be increased to any thickness, and modifications in the solution and process allow of a large number of variations being made in the colour of the deposit.

Metal Content of Solutions.—The strength of a gilding solution is controlled considerably by the high cost of the metal. In most cases of deposition we aim at a high metal content, but the outlay necessary in the case of gold sets a somewhat narrow limit. Solutions are sometimes made up to about 2 ozs. of the metal per gallon; but they are more commonly much weaker than this. Indeed, solutions containing but a few dwts. of the metal yield satisfactory deposits. In the following methods of preparation, therefore, the gold or gold compound may be considerably diminished in quantity without appreciably altering the quantities of the other constituents.

Preparation of Solution.

Electrolytic Method.—This method has previously been referred to. While not very suitable for other metals, with perhaps the exception of silver, it is particularly serviceable for gilding solutions. From $\frac{1}{2}$ to 1 lb. of best cyanide is dissolved in a gallon of water. A little of the solution is introduced into a clean—preferably a new—porous pot, in which a copper or carbon plate serves as cathode. The porous pot is then stood in the main solution. A piece of fine sheet gold, hung in the larger bulk of KCN solution, is made the anode. By the action of the current, gold dissolves from the anode, and the process can be continued until the requisite amount of gold has disappeared into the solution, this being found by weighing the plate. As some slight diffusion of the gold solution through the porous pot occurs, it is well to replace the solution in the pot by fresh cyanide solution, the first charge being poured into the main solution. By this method a gilding solution of any strength is obtained, and the process may be continued until the solution is found to yield a good deposit.

Chemical Methods.—(1) Following the method recommended for a silver solution, a solution of potassium cyanide is added to a solution of the required amount of gold as chloride, a little at a time, with stirring, and allowing the precipitate formed to settle. The precipitate has a brownish colour, and is gold cyanide. The addition of KCN is continued until no more precipitate is formed. As with silver, an excess of KCN must be avoided, the precipitate being soluble in excess of KCN. Should excess of KCN be added inadvertently, its effect may be counteracted by adding a little more gold chloride solution. The precipitated gold cyanide is allowed to settle, and the clear liquid poured off into a vessel in which it can be preserved for the recovery of any gold which it may contain. The precipitate is washed with water once or twice, saving the wash-water on account of small particles of precipitate which it may contain. The washed precipitate is now dissolved in more KCN, with an allowance for free cyanide, and made up to its proper bulk with distilled water.

(2) A variation of the above method involves the precipitation of the gold from the chloride solution by means of ammonia. As the precipitate is soluble in excess of ammonia solution, care must be exercised in order to avoid such an excess. The precipitate is now washed with water and dissolved in potassium cyanide solution with a sufficient allowance for "free" KCN. A further warning must be made against allowing the ammonia precipitate to dry, as when dry it is exceedingly explosive.

(3) Many other recipes and formulæ are available for the preparation of gilding solutions, in which other compounds are introduced, often in considerable quantities. It must be remembered, however, that the simpler the composition of the solution, the less likely is error to occur, and, if such should happen, the more easily can it be rectified. A word of warning is therefore urged against so many solutions of such fanciful and complex composition.

Working the Solution.—A gilding solution is liable to perhaps more variation than any other solution. Slight changes in current, temperature, metal content, and presence of other metals make a decided impression on the character of the deposit. This prevents too rigid rules and regulations being laid down to guide the operator. A little experience is worth much detailed instruction, but the following points may be taken as guides.

(1) **Temperature.**—The temperature of a solution very considerably alters the working. Gold solutions are usually worked warm. If cold, then they should contain more gold. Warming a solution decreases the resistance and increases the current. Changes of colour of the deposit, with changes of temperature, may be due to the change of current accompanying the change of temperature. Generally, a warm solution gives a warmer tone to the deposit, the deposit usually being pale in a cold solution.

(2) **Current.**—Low current density produces pale deposit. Higher current density produces a more pleasing colour. When the C.D. is excessive, the deposit becomes dark brown or "foxy." The articles should then be removed, rinsed, scratch-brushed, and again put into the solution with a lower current. An improvement in the colour can also be effected by the motion of the work, this being equivalent to the ordinary beneficial effect of agitation.

(3) **Anodes** should be of fine sheet, preferably annealed. There is more necessity for a gold anode to be pure than for a silver anode in the silver bath. It may be suspended either by a gold or platinum wire. A simple arrangement for raising or lowering it in the solution is an advantage, as some easy control over the current, and consequently the colour of the deposit can be effected by lowering the anode with more work in the bath, and *vice versa*. A somewhat dark deposit can, after scratch-brushing, be remedied by slightly raising the anode out of the solution. The anode should dissolve freely under the influence of the current, and as it dissolves appreciably

in the cyanide solution even without the current, it should be removed when not in use. Some gilders, especially for cheap work, prefer to use a platinum anode, and supply the gold to the bath by frequent small additions of gold chloride. This, however, is not the best method. Uniformity of colour is best attained with uniform conditions, including that of metal content.

(4) **Cyanide.**—A gold solution may contain free cyanide within very wide limits. There should, however, at least be sufficient to keep the anode clean. On the other hand, an excess is not of great inconvenience, as it only involves more gas being given off at the cathode without much change in the character of the deposit of gold.

(5) **E.M.F. and Current.**—It will by now be quite understood that, with solutions differing widely in metal and cyanide content, sometimes warm and sometimes cold, no very definite E.M.F. and current density can be stated, and it is unwise to attempt to give any figures. Each solution differs from others sufficiently to prevent any one figure being applicable to all solutions. Then, again, work for gilding is usually so irregular in shape that even a rough idea of its area is difficult to obtain. Better by far, then, determine the conditions which yield satisfactory results in a solution, and then attempt to maintain them.

(6) **Wire-marks** are usually pronounced in gilding. These may be removed by light scratch-brushing, after which, the wire should be attached in another position.

(7) **Thick deposits**, when required, are best obtained by frequently scratch-brushing. This removes any little irregularities in the deposit, which is thus kept more uniform.

(8) **Quicking** is also resorted to, in order to ensure thicker deposits which shall still be adhesive, but this should not be essential.

(9) **Rinsing** should be very systematically done. Each article removed from the bath is covered with gold solution. Many articles entering the bath are covered with water. The

bath is therefore being weakened, and unless precaution is taken, gold is being lost. A bowl of rinsing water should be kept near the gilding bath, and all work removed from the bath should be passed through it first. After a time this water can be put aside for the recovery of gold. Again, after scratch-brushing work, the greatest care must be taken to ensure complete rinsing before re-immersing the work in the vat. If scratch-brush liquor finds its way into the bath, it leads to a darkening of the deposit, which cannot be remedied by scratch-brushing or varying the current. If the trouble assumes serious proportions, then it will necessitate either recovering the gold from the bath, or some similar method of getting rid of the impurity.

Colour of Gold Deposits.—It has already been pointed out that a pure gold solution may yield a deposit of metal varying from a pale yellow colour to the brown or foxy deposit, such variations being brought about by conditions of current, temperature, motion, etc. Other variations, however, are possible by contamination with other metals, chiefly copper and silver, and, unless specially required for the effects they produce, these metals should be entirely absent from the solution.

The addition of copper cyanide introduces a redness into the deposit. This heightened colour is often required, but in attempting to produce it, the copper cyanide solution should be added most sparingly, and the amount increased if necessary. Too much copper cyanide will give a coppery appearance, far from pleasing. Similarly, the addition of silver cyanide (or good silver-plating solution) gives a faint green tint to the deposit. The colour of a deposit is also heightened by a deposit of copper below it, and for gilding on silver this course is to be recommended, as for only a very thin coating of gold the whiteness of the silver considerably lessens the colour of the film of gold.

Dead Gilding.—An excellent result can be obtained by depositing gold on surfaces already "dead." Such surfaces

may be produced by sand-blasting, dipping, or by depositing a film of copper from the acid bath. Whichever method is adopted the utmost care must be taken to avoid the slightest rubbing, either before or after gilding.

The deposition should proceed easily and uniformly, using current conditions which will at once produce the colour desired in the finished work. Subsequently, the work should be most thoroughly rinsed in cold and hot water, and dried through sawdust without rubbing.

Stripping Gold Deposits.—The stripping of a metallic deposit is a process governed by laws, and according to the metal to be removed, and also to the basis metal—so must the “strip” be chosen. Now, gold is not soluble in any of the ordinary acids singly, and for chemically stripping gold a mixture of the *aqua regia* type may be used. The clean, dry work is put into a mixture of hydrochloric and nitric acids, in the proportion of three or four to one respectively. Silver in this liquid would be slightly attacked, but not dissolved. Brass and German silver would suffer some corrosion. The solution, therefore, requires careful watching, and the work should be withdrawn occasionally, well rinsed, and examined. If the stripping is incomplete, the work should be drained or dried, and re-immersed, the operations being repeated till the gold is entirely removed. A safer method, and one that is applicable also for the removal of gold from the inside of cups, basins, and similar articles is to make the work to be stripped the anode in a solution of potassium cyanide, using a piece of iron for cathode. In the case of a jug or basin, the vessel serves to hold the electrolyte. Other metals will also be dissolved, and due care should be taken, although, as the amount of gold to be removed is usually small, corrosion to the base metal is very slight.

CHAPTER XVIII

Electro-Brassing

Electrolysis of Mixed Sulphates of Zinc and Copper.—If the deposition of a metal from one of its solutions is regarded as a simple problem, the deposition of two metals simultaneously may be expected to introduce some difficulties. For example, if to an acid copper solution some zinc sulphate solution is added, no change in the deposit occurs, even though large quantities of zinc are present. It may, perhaps, be argued that zinc is in all probability deposited with the copper, but in so small a proportion that only analysis will detect it. Now, analysis shows that if the solution is decidedly acid, no zinc occurs in the deposit of copper. Such a solution is therefore useless for the purpose of depositing an alloy of zinc and copper. It provides, however, an excellent method for separating the two metals, for from an acid solution of the sulphates or nitrates of the metals, the whole of the copper can be deposited and weighed, while the zinc remains in the solution, and the method is of considerable analytical importance. Further, the difficulty of depositing the metals simultaneously from such a solution is applied in the process of electrolytic refining of copper, already referred to on p. 180. Indeed, when we remember the ease with which zinc displaces copper from the sulphate, it would hardly be reasonable to expect zinc to be deposited from a solution containing copper sulphate.

The Mixed Cyanides of Copper and Zinc.—In Chapter XIII. much has been said with reference to the

deposition of copper from the cyanide solution. With very little exception it applies also to the deposition of zinc from zinc cyanide solution. The double cyanide of zinc and potassium $[\text{Zn}(\text{CN})_2 \cdot 2\text{KCN}]$ is soluble in water, while the single cyanide is not. It undergoes the same type of decomposition, 2K passing to the cathode and depositing zinc, thus—



while $\text{Zn}(\text{CN})_4$ passes to the anode, and, taking up more zinc, forms $2\text{Zn}(\text{CN})_2$, which must be dissolved from the anode by free cyanide. The methods of producing quantitative deposits are identical with those for copper, but the zinc is deposited in the usual proportion in which it dissolves in the Daniell cell when $31.8 \text{ Cu} \equiv 32.5 \text{ Zn}$. Again, copper cyanide is much more stable than the sulphate, and for this reason is not decomposed by iron and only slowly by zinc. The stability of zinc cyanide is also a little greater than that of the sulphate. Hence, in the mixed cyanides of copper and zinc we have compounds which are more nearly alike in their degree of stability, and which are therefore capable of simultaneous decomposition with the deposition of the mixed metals. Of the two metals, copper is the more easily deposited, and in attempting to produce the alloy allowance has to be made for this fact.

Preparation of Solution.—To the detailed description given in Chapter XIII. of the methods of preparing copper cyanide solutions, little need be added. To produce a good brassing solution the same methods may be followed, but instead of starting with copper sulphate, the same weight of a mixture of copper and zinc sulphates, or carbonates in which the two substances are in like quantity, may be used.

The zinc sulphate goes through the same reactions as the copper sulphate, except that there are no colour changes. These, however, are not required, as the completion of the changes is indicated by the coloured copper compounds present. Then in Method I., for copper cyanide (p. 183)

8 ozs. each of copper and zinc sulphates may be used, and the preparation completed as there instructed. In Method III., for copper, as on p. 185, a brassing solution results by dissolving the mixed carbonates. Usually the metals or salts in the same amount are taken.

The solution when prepared is used with a brass anode in exactly the same way as for copper, and no difficulty will be experienced in obtaining a good yellow deposit. To persistently maintain a required shade of brass is, however, a more difficult matter, as many conditions, some of which require careful control, influence the composition and colour of the deposit. These conditions are treated further on in this chapter.

Composition of Deposited Brass.—Brass is an alloy of approximately 66 parts of copper and 34 parts of zinc. It has a good yellow colour. If the proportion of copper is sensibly increased, the alloy acquires a reddish tinge. Similarly, with a larger proportion of zinc, the alloy becomes whiter till the alloy containing equal parts of the two metals is practically white. For all ordinary purposes the composition of a brass deposit must range closely round the $2\text{Cu} : 1\text{Zn}$ proportion. Now, such a proportion is not necessarily obtained in the deposit by using this proportion of the two compounds. It is far more common to use a distinctly larger proportion of the zinc compound. Of the two compounds the copper salt is more easily decomposed, and therefore if the two compounds are present in about the same quantity, a larger share of the current will deposit copper. Another point, however, must be noted here. The proportion of copper and zinc deposited from cyanide solutions is as 63.6 to 32.5, or roughly as $2 : 1$. Hence, if the current were divided fairly equally between the two compounds, the deposit would be of the ordinary $2\text{Cu} : 1\text{Zn}$ composition, and this condition is attained when a brass of ordinary composition is obtained. In order to get such an equal distribution of the current it is necessary to have at least as much zinc (if not more) in the solution as copper. The

following table (XXII.) shows the distribution of the current through the two compounds for different compositions of deposit, assuming that no hydrogen appears :—

TABLE XXII.
SHOWING PROPORTION OF CURRENT DEPOSITING COPPER AND ZINC
IN BRASS DEPOSITS.

Brass.		Percentage of current depositing	
Percentage of copper.	Percentage of zinc.	Copper.	Zinc.
100	0	100·0	0·0
90	10	82·2	17·8
80	20	67·2	32·8
70	30	54·4	45·6
60	40	43·4	56·6
50	50	33·8	66·2
40	60	25·3	74·7
30	70	17·9	82·1
20	80	11·3	88·7
10	90	5·3	94·7
0	100	0·0	100·0

The conditions which alter the colour of the deposit are the conditions which alter this proportioning of the current.

Conditions affecting the Composition of the Brass Deposit.

(a) Proportion of the Zinc and Copper Compounds.—

This effect will be at least qualitatively obvious. Quantitatively the effect is still more striking, for from a solution containing the zinc and copper compounds in the proportion of 10 equivalents of zinc to 1 equivalent of copper, it is easy to produce a deposit containing the two metals in about the same quantity; while solutions containing quite a fair proportion of zinc compound may yield deposits with a high percentage of copper.

(b) **Strength of the Solution.**—All other conditions being the same, the mere fact of diluting a solution renders the deposition of zinc easier. This is illustrated in a case where a solution was diluted with its own bulk of water and thereby brought down to half strength. All other conditions were kept constant.

TABLE XXIII.

EFFECT OF DILUTION OF SOLUTION ON COMPOSITION OF
ELECTRO-DEPOSITED BRASS.

Experiment.	Percentage of Cu in deposit.	
	Strong solution.	Dilute Solution.
1	93·5	86·6
2	92·2	71·0
3	68·3	56·7
4	63·8	59·4

Higher C.D.'s were used in the successive experiments. A solution which has, through being kept warm, become boiled down, may thus give a reddish deposit which may be changed to yellow by merely making up to the original bulk with water.

(c) **Effect of Current Density.**—If of the two metals one is deposited more easily, it is to be expected that low current densities will favour its deposition in larger proportion, while higher C.D.'s will yield a larger proportion of the less easily deposited metal. This is amply shown in the figures in Table XXIV. (p. 246) taken from actual experiments :—

Hence, increasing the current on the same cathode surface tends to the production of a yellower deposit.

(d) **Effect of Temperature.**—This is also very marked, as the following figures from experiments show. It must, of course, be understood that when an effect of this kind is being investigated, all other conditions, such as current density, strength of solution, etc., are kept quite constant, so that

TABLE XXIV.

EFFECT OF CURRENT DENSITY ON COMPOSITION OF ELECTRO-DEPOSITED BRASS.

Experiment.	Current.	Deposit.	
		Percentage of Cu.	Percentage of Zn.
1	1.0 amp.	94.3	5.7
2	1.5 "	84.8	15.2
3	2.0 "	72.8	27.2
4	2.5 "	68.0	32.0
5	3.0 "	65.5	34.5

whatever change is observed may be reasonably attributed to the changing condition.

TABLE XXV.

EFFECT OF TEMPERATURE OF SOLUTION ON COMPOSITION OF ELECTRO-DEPOSITED BRASS.

Experiment.	Temperature ° C.	Percentage of Cu in deposit.
1	60	94.5
2	50	92.0
3	40	87.8
4	30	86.0
5	20	81.0

Workshop experience also shows, by merely glancing at the colour of the deposit, that a yellower alloy is obtained in the cooler solutions.

(c) **The Effect of Free Cyanide** is marked in the direction of producing reddish deposits, that is, of facilitating the deposition of copper, and the effect is strikingly increased with the addition of further amounts of free cyanide. This is shown by the following figures:—

TABLE XXVI.

EFFECT OF FREE CYANIDE ON COMPOSITION OF ELECTRO-DEPOSITED BRASS.

Current (amperes).	0.5	1.0	1.5	2.0	3.0
Percentage of Cu { No free KCN	93.5	92.2	68.3	63.8	59.3
{ Free KCN	94.3	92.7	91.2	92.6	92.5

It is thus seen from many experiments in which the deposits of brass were subsequently analyzed, that the composition of the brass depends upon a number of conditions, and within a wide range of conditions a good colour can be obtained. Further, if the colour is unsatisfactory, for example, too red, then it may be improved by (1) adding more zinc cyanide, (2) diluting, (3) cooling, or (4) increasing the current. The addition of zinc carbonate has the 'double effect' of increasing the amount of zinc present and reducing the free cyanide. One other condition which greatly influences colour is the addition of ammonia either as the solution or solid carbonate. The zinc constituent of a brassing solution is less soluble than the copper. It may therefore separate to some extent to the bottom of the vat. The zinc content of the solution is thereby diminished, and may be restored to its original value by the addition of some substance, preferably other than cyanide, which will dissolve this deposit. This is done by ammonia, and hence the change of colour.

Quantitative Deposition of Brass.—With single metals it is a simple matter to calculate the weight of the metal which should be deposited per ampere-hour. This has already been done in several instances. The case of an alloy is more complex, especially as so many circumstances affect the composition of the alloy. To approach this matter simply, let it be assumed that brass is being deposited in a circuit which contains a copper voltameter in series. Assume next that in depositing the brass no hydrogen is evolved. The conditions

to ensure this can be attained without much difficulty. If we have now a "brassing" solution of such extreme composition that only copper is deposited, then such a "brass" (which is really only copper) will weigh twice that of the copper deposited in the voltameter. If, on the other hand, the brassing solution is of such extreme composition that only zinc is deposited, then the weight of such a "brass" compared with the weight of copper from the voltameter will be as 32.5 : 31.8, or as 1.022 : 1. With a solution yielding a deposit of both copper and zinc, then—

$$\frac{\text{weight of brass}}{\text{weight of Cu from voltameter}}$$

will be less than 2 but greater than 1.022, and for every different composition of deposited brass there will be a definite relation between the weight of brass and the copper deposited in the voltameter. This relation is found as follows:—

Assume the composition of the brass deposit to be 50Cu : 50Zn. Then—

$$50\text{Cu (from cyanide)} \equiv \frac{50}{2} = 25\text{Cu from acid solution}$$

$$\text{also } 50\text{Zn} \equiv \frac{50 \times 31.8}{32.5} = 49\text{Cu from acid solution}$$

$$\therefore \frac{50\text{Cu} + 50\text{Zn}}{100 \text{ brass}} \equiv 74\text{Cu from voltameter}$$

$$\therefore \frac{\text{brass}}{\text{Cu from voltameter}} = \frac{100}{74} = 1.35$$

Again, for brass of composition 66Cu : 34Zn—

$$66\text{Cu (from cyanide)} \equiv 33\text{Cu from voltameter}$$

$$34\text{Zn} \equiv \frac{34 \times 31.8}{32.5} = 33.3\text{Cu from voltameter}$$

$$\therefore \frac{66\text{Cu} + 34\text{Zn}}{100 \text{ brass}} \equiv 66.3\text{Cu from voltameter}$$

$$\therefore \frac{\text{brass}}{\text{Cu from voltameter}} = \frac{100}{66.3} = 1.51$$

The following table shows the ratios calculated for other compositions :—

TABLE XXVII.

RATIO $\frac{\text{BRASS}}{\text{COPPER FROM VOLTAMETER}}$ COMPARED WITH
COMPOSITION OF DEPOSIT.

Composition of brass.		Brass Copper from voltameter
Percentage of Cu.	Percentage of Zn.	
100	0	2.00
90	10	1.825
80	20	1.678
70	30	1.550
60	40	1.445
50	50	1.350
40	60	1.269
30	70	1.195
20	80	1.130
10	90	1.073
0	100	1.022

These figures are plotted in the curve shown in Fig. 107, and from this curve the approximate composition of the brass deposit for which the ratio is known can be easily found, always on the understanding that no hydrogen has been deposited. If hydrogen is evolved, then the figures obtained from such a table or curve are of no value except that they indicate values of copper which must be exceeded, and values of zinc which cannot be exceeded. The matter is one of some interest, as it is tolerably easy to obtain conditions under which little or no hydrogen is evolved.

Further, if the ratio of the weight of the brass deposit to that of copper in the voltameter is known, the percentage of copper in the deposit can be calculated from the following expression :—

$$\text{Percentage of copper} = \frac{204}{R} (R - 1.022)$$

where R is the ratio of brass to copper in the voltameter.

Anode Corrosion.—In depositing an alloy, anodes of the composition of the alloy may be used, or even separate anodes of the two metals. The latter method is open to the disadvantage that the more positive metal (zinc in this case) will

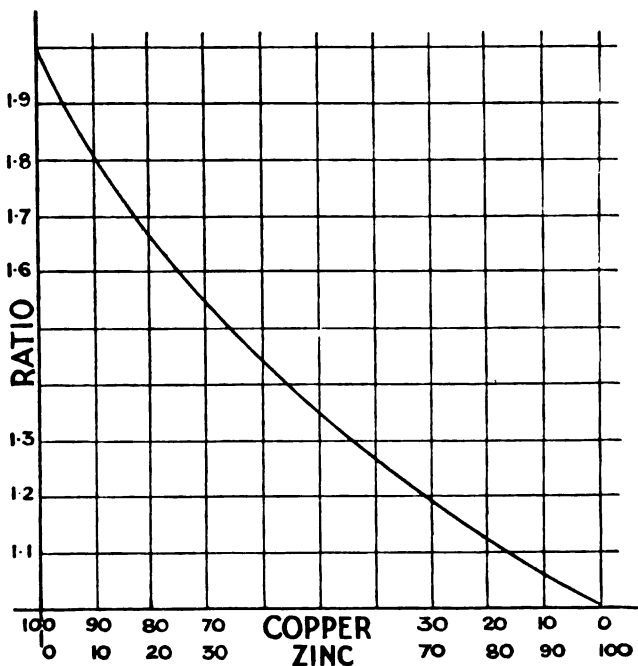


FIG. 107.—Showing relation between composition of a brass deposit and the ratio $\frac{\text{copper from voltameter}}{\text{zinc from voltameter}}$

corrode more rapidly than the less positive metal, and their proportion in the solution is thereby modified. Some allowance can be made for this by reducing the area of the zinc anodes—that is, increasing the share of the current which passes from the copper anodes. More uniform working is obtained, however, by using an anode of the alloy, when, *if* one metal

dissolved away more rapidly than the other, it would expose a larger area of the other metal for corrosion. In any case the solution could be enriched with either metal by adding anodes of that particular metal.

Another point which may be noted is the fact that during anodic solution, zinc and copper demand different amounts of cyanide, and hence, if the two metals are dissolved in a proportion different from that in which they are deposited, the change of composition of the solution affects the free cyanide as well as the metals. Thus—

To convert Zn into $\text{Zn}(\text{CN})_2$, $\overset{65}{\text{2 KCN}}$ requires $\overset{(4 \times 65)}{4 \text{ KCN}}$

To convert Cu into $\text{Cu}(\text{CN})_2$, $\overset{63.6}{\text{KCN}}$ requires only $\overset{(2 \times 65)}{2 \text{ KCN}}$

Approximately, therefore, zinc requires four times its weight of cyanide and copper only twice its weight.

Similarly, on decomposition, these proportions of cyanide would be liberated. Now, if excess of zinc is being dissolved and excess of copper deposited, more cyanide is required for the solution of the zinc than is liberated by the copper, and the free cyanide is thereby diminished. Thus the reactions taking place in a mixed solution are complex, and for uniform working, uniform conditions must be maintained.

The Process of Deposition.—Little need now be said about the actual process of electro-brassing. The conditions controlling it have been considered, and the application of these principles to the actual deposition is a matter of practice and experience. Further, after what has been said about the process of depositing copper from the cyanide solution, there remains only the necessity of emphasizing some of those remarks in their application to brassing. In the first place, the process requires careful control. There is no natural tendency for the colour to remain absolutely of any required shade, or for the conditions to automatically adjust themselves, and the different conditions require some sort of balancing one against

the other. While a good deposit may be obtained with a cold stationary solution, there is greater ease of control with a warm agitated solution, though this may not always be possible. Anodes should be kept clean. Strictly speaking, they should *keep* clean in the process, but this does not always happen. An occasional scouring with sand or pumice stone serves to detach any cyanides which may have accumulated on them. As the solution evaporates, frequent additions of water should be made. If giving a red colour, the solution may be improved by the addition of more zinc compound, or without this, ammonium carbonate may suffice. Even when the two metals are being deposited in a correct proportion an excessive C.D. may give rise to burning, yielding a dark powdery deposit on the edges of the work.

Work for electro-brassing is prepared in the same way as for cyanide coppering, and the process is used to produce heavy deposits of brass on iron bedstead and fender work, when deposition is allowed to proceed slowly during the night. The deposits may subsequently be polished and lacquered.

Deposition of Bronze.

The methods of depositing two metals simultaneously are of application for the production of other alloys, of which bronze is a good example. Bronze is an alloy of copper and tin in the proportion of about 90 : 10, though the term is also used to represent a whole series of alloys in which the tin may vary from 5-20 per cent. Solutions for depositing brass are made by mixing solutions of copper and zinc cyanides in suitable proportion. For the deposition of bronze, however, the solutions usually employed for copper and tin separately are not of like composition, and an electro-bronzing solution is therefore not so readily prepared. Tin can be deposited from the chloride, stannate, thio-stannate, pyrophosphate, or oxalate solutions. A copper

solution is therefore required which can be freely mixed with one of these solutions. For this purpose the sulphate, chloride, or cyanide solutions are not suitable. Double oxalates of the two metals, with ammonium oxalate, can be mixed, and yield a good bronze deposit. The following proportions are suitable:—

Copper Solution.

(1) 1 oz. copper sulphate dissolved and made up to 20 fl. ozs.

(2) 2 ozs. ammonium oxalate } dissolved and made up to
 $\frac{1}{4}$ oz. oxalic acid } 20 fl. ozs.

Solution (2) is then slowly added to solution (1), shaking after each addition. A light green precipitate first forms, but dissolves on further additions of (2).

Tin Solution.

(1) 1 oz. tin protochloride (SnCl_2) dissolved and made up to 20 fl. ozs.

(2) 2 ozs. ammonium oxalate } dissolved and made up to
 $\frac{1}{4}$ oz. oxalic acid } 20 fl. ozs.

Again, add solution (2) to (1), shaking after each addition, until the whole has been added.

The tin and copper solutions can now be mixed in the proportion of 2Cu : 1Sn, some of each solution being kept in reserve for addition if occasion arises. The mixed solution now contains about the same weights of the metals. The solution may be worked cold or warm with a bronze anode, and of the two metals, tin is the more difficult to deposit. To ensure its deposition, methods similar to those already described for brassing should be followed.

Deposition of German Silver.

This alloy consists of copper, zinc, and nickel in varying proportions, a usual composition being 60Cu : 24Zn : 16Ni. The cheaper qualities contain more zinc and less nickel. In choosing a solution from which the alloy may be deposited,

it may be noted that cyanide solutions of nickel can be prepared in a similar manner to those of copper and zinc, and a mixture of the three cyanides can therefore easily be made.

A solution may also be made by dissolving a sample of the alloy in nitric acid, evaporating off excess of acid, and precipitating the carbonates with washing-soda or potassium carbonate. The washed precipitate, which consists of the three carbonates, can then be dissolved in cyanide, the solution being worked with an anode of the alloy.

CHAPTER XIX

Metal-Colouring

Oxidation and Tarnishing of Metals.—There are very few metals which, when polished and exposed to air, retain their lustre and surface for any length of time, and they are chiefly the noble metals, including gold and platinum. All the more common metals, as iron, copper, zinc, silver, and lead, soon become dull, and their surfaces, once smooth, become rough and corroded. The problem of preserving the surface and lustre of a metal or deposit is, therefore, one of importance. Metals which have undergone surface alteration, such as discolouring, are said to be tarnished, but the terms “oxidized” and “oxidation,” while used in a very wide sense, ought strictly to refer to actions which take place through the medium of oxygen.

Composition of Air.—Air contains two chief constituents—

(1) **Oxygen**, an active agent promoting tarnishing and corrosion. It constitutes about 21 per cent. of the air by volume.

(2) **Nitrogen**, to the extent of about 79 per cent. by volume. It is an inactive element, and plays no part in the usual actions attributed to air.

In addition to these there are a number of substances occurring in small quantities, but playing a very large part in the corrosion of the metals. They are—

(3) **Water vapour**, produced by the evaporation of all exposed water.

(4) **Carbonic acid gas**, or carbon dioxide (CO_2) generated by the combustion of all carbonaceous materials, including the foods we eat.

(5) **Sulphuretted hydrogen** (H_2S), due to the presence of sulphur in coal gas and coal, and to the decay of vegetable and animal materials containing sulphur.

(6) Many acids in small amounts—such as nitric acid, which is produced during thunderstorms, and sulphuric acid produced by burning coal containing even small amounts of sulphur. The amount of sulphuric acid turned in the atmosphere on this account is astounding, in view of the large amount of coal consumed (often so inefficiently) in large manufacturing towns. Naturally the atmosphere in some localities is very bad. In the neighbourhood of a gas works, or chemical works, large amounts of impurities are turned out into the air, some of which are easily recognized by their odours. Stringent Board of Trade regulations have done much to minimize the evil. Coming down to still more local circumstances, the atmosphere of a chemical laboratory or a plating and dipping workshop is certainly not conducive to the permanence of the surface of a lustrous metal, and steps must be taken to preserve such metals.

Oxidation of Metals.—Most metals combine readily with oxygen, forming oxides. Gold, silver, and platinum are notable exceptions. These oxides are of different colours. Copper oxide (CuO) is black, iron oxide (Fe_2O_3) is red, while cuprous oxide (Cu_2O) is red, and iron scale (Fe_3O_4) is black. They are formed with different degrees of ease. Some metals, like sodium, magnesium, and zinc, readily burn in air, and form oxides. With copper and iron the oxidation is slower. In general, an easily oxidizable metal is plated with a less oxidizable metal. Another factor, however, enters into the rate of oxidation. If an oxide is formed as a permanent film, adherent and not easily detached, it protects the metal from further oxidation. Both magnesium and aluminium are prevented from rapidly oxidizing in air by such a protective layer,

and the difficulty attached to the plating of aluminium is connected with this layer of oxide. This being so, why not purposely cover some of the metals with oxides and thus prevent further oxidation? This is in fact the aim in many methods of metal-colouring and bronzing, such surface coverings being selected as will combine efficiency, permanence, and, so far as possible, enhance the appearance of the metal. Similar remarks could also be made with regard to other compounds—notably the sulphides, which are produced as thin films in the colouring of copper and silver.

Prevention of Oxidation, etc.—Very many methods are available, and may be briefly summarized as follows :—

I. Coating the metal with a layer of protective paint, varnish, or lacquer. The success will obviously depend much upon the perfect continuity of the covering, otherwise corrosion occurs at an exposed portion and goes on underneath the layer.

II. Coating the metal with a layer of less oxidizable metal. This is done in—

(A) **Galvanizing**, in which iron and steel are covered with a thin layer of zinc by passing through a bath of molten zinc, or by embedding in a bath of zinc dust, and raising the temperature to about $200-300^{\circ}\text{C}$., as is done in “Sherardizing.”¹

(B) **Tinning**, a similar method of protecting iron and steel by a layer of tin.

(C) **Electro-deposition**, comprising most of the usual plating processes.

(D) **Simple Immersion Processes**, in which metal is deposited without the aid of externally produced current. This is done in tinning small brass articles in the oxalic acid and tin bath, in silvering clock and instrument dials with powders or pastes, or in “steel” bronzing, where arsenic compounds enter into the composition of the “bronze,” the arsenic being deposited upon the metal surface.

¹ *Electro-chemist and Metallurgist*, vol. iii. p. 828.

III. By covering the metal with a permanent layer of oxide, sulphide, or other compound. Such a protective layer may, and often does, need further protection from the changes which it might slowly undergo by long contact with a corrosive atmosphere. Different methods of applying this principle are—

(1) The Bower-Barff process for protecting iron by heating it in superheated steam, thus forming a layer of black oxide (Fe_3O_4).

(2) The many and varied methods of slow oxidation by raising the temperature of the metal to produce slow and easily controlled oxidation.

(3) By passing the metal through some chemical solution by the action of which a perfect and uniform layer of the compound may be produced. This is usually followed by lacquering.

It is chiefly to this last method that attention is now directed, a few such solutions being given together with some precautions necessary for success. Special treatises can then be consulted.¹

Principles of Chemical Metal-Colouring.—Many metals, when immersed in certain chemical solutions, assume colours of more or less pleasing effect. These colours are due to the formation of films of compounds, such as oxides and sulphides, upon the metal. Each compound has, in the first place, its own distinctive colour. This colour is, however, dependent to some extent upon the method of formation, and also upon its thickness. It is modified by the colour of the metal beneath it, and when it is remembered that the film may be produced either dull or with a lustrous finish, it will be seen that metal colouring lends itself to endless variety. An illustration of the variety may be seen by heating a piece of polished copper in a non-luminous flame. A black deposit is produced where the temperature is highest. Further from the flame the deposit becomes lighter, passing from the dull

¹ See Hiorns, "Metal Colouring and Bronzing." Macmillan & Co.

black (CuO) through a gradually lighter brown to the cooler portions, where only red oxide (Cu_2O) has been formed. Similarly a piece of copper exposed to sulphuretted hydrogen will assume, according to the length of exposure, every shade from the red colour of the metal through the different shades of brown to black. In these cases the film is due to combination of the copper with oxygen or sulphur. In many cases, however, where the colour is produced in a solution it is due to corrosion, and a loss of weight can readily be traced.

Necessity for Uniform Conditions.—In the case of heating copper, it will be apparent that a uniform effect can only be hoped for by maintaining a uniform temperature, for the rate of combination of copper and oxygen is considerably promoted by a rise in temperature. This is an essential which cannot be too strongly emphasized. It is difficult to obtain uniform results where only small quantities of liquid are being used, for in the course of use they alter in composition, and therefore in the shade of colour which they may produce.

Colouring Base Metals.—All metals do not lend themselves to these chemical colouring processes with the same ease. Copper is a metal particularly adapted for the purpose of metal-colouring, and a wide variety of effects can be produced upon it. Metals like iron, tin, and zinc do not so readily respond to the metal-colouring processes, but the difficulty in colouring them may be surmounted by coating them with copper by the electrolytic process, after which they may be treated as copper. It must be remembered, however, that the colouring process is often one of corrosion, and a sufficient allowance of copper must be made to withstand this corrosion.

Effect of Impurities.—A comparison of the results obtained upon copper and brass in any solution will at once reveal the profound effect of impurities. Some difference can easily be understood in the case of copper and brass, where the latter contains as much as 34 per cent. of zinc; but the differences which are obtained between two specimens of brass

of slightly varying composition, or between two samples of copper, one pure and the other of an ordinary grade, are, to say the least, astounding. It is characteristic of impurities that they very considerably modify the properties of the metals when present in only small quantity, and in this modification of the colours produced in these chemical processes the rule is rigidly adhered to. This at once accounts for the difficulty experienced in continually producing a uniform shade or colour upon a variety of brass articles manufactured from different samples of metal.

Cleanliness Essential.—For successful metal-colouring, cleanliness is essential, as much so as in plating. All metals before being subjected to the metal-colouring process should be thoroughly cleaned by the usual processes. No trace of grease or tarnish—not even a finger stain—should be present, and in many cases even greater care is necessary than in the ordinary plating process. Apart from such scrupulous cleanliness, good uniform results cannot be obtained, and the colours must be entirely removed and a fresh start made. For the methods of cleaning the different metals reference must be made to Chapter IX., dealing with the processes preparatory to plating.

Parcel Metal-Colouring.—The fact that no two metals will give the same effect in any given solution, or that in some solutions one metal may be satisfactorily coloured while another is practically unaffected, may be applied with considerable advantage in colouring “parcelled” work. Thus copper and brass behave very differently in many solutions, there being in some cases a marked contrast in the colours which they assume. Again, as partial colouring can also be effected by judicious “stopping off,” still greater variety can be produced by obtaining, if required, colours on only portions of the work. Much depends upon the artistic sense of the operator.

Relieving.—In other cases pleasing contrasts can be obtained on work in which some parts are fairly prominent, by first colouring the whole of the surface and then removing

the colour from the more prominent portions by rubbing with sand or pumice. At first the result may look somewhat crude, but more finish can be obtained by passing the work momentarily through the colouring solution. In some cases a sufficient contrast may be obtained by more severely scratch-brushing the prominent parts. This throws these parts into greater relief and contrast with the darker background.

Again, further effects can be produced by burnishing the prominent parts and sandblasting the background of a piece of work. After carefully cleaning and immersion in the colouring solution, the roughened parts look much darker than the smoother portions.

In the case of large work which cannot conveniently be immersed in a solution, the colouring solution may be applied with a soft brush, and this admits of some parts receiving greater exposure to the colouring compound than others.

Lacquering.—Finally, though by the metal-colouring process, films of compounds are produced which, in comparison with the original metal, are very permanent, still, in course of time these deposits in a corrosive atmosphere would undergo discoloration. It is usual, therefore, to lacquer them, and this should be done with colourless lacquers in order not to interfere with the colour of the film. Where, however, uncoloured metal is exposed, coloured lacquers are commonly used, such, for example, as those which give the well-known golden tint to brass and the enhanced copper colour to plain polished copper work. The lacquering process needs no description; a little practice under an experienced operator is worth far more than a whole volume of hints, and to some extent this remark also applies to some of the methods now to be described.

Methods of Metal-Colouring.¹—These are so very numerous that classification within the compass of so short an account becomes almost impossible. A few instances only of

¹ A somewhat wider meaning is given to this term than to that of "bronzing."

some of the mixtures which give pronounced results will be given under the following headings :—

- (a) Deposition of metals by simple immersion, and
- (b) Production of coloured films.

Colouring by Simple Immersion Deposition.—The principle of these methods is the simple replacement of the metal in the solution by the metal under treatment. The deposited film is in any case only thin, and cannot be appreciably thickened by long-continued immersion.

The Use of Arsenic and Antimony Compounds is frequently resorted to on account of the ease with which these metals are turned out from their solutions, and of their non-liability to tarnish.

Rx.	White oxide of arsenic (As_2O_3)	30 grams
	Hydrochloric acid (strong)	50 c.c.
	Water	250 c.c.

The oxide is first readily dissolved in the acid by warming, and the solution diluted with the water. The quantities used are open to wide variations, with corresponding changes in the ease and rapidity of the deposit. The solution works more rapidly when stronger and warm, and more slowly on cooling or diluting. In this solution brass and copper receive a steel-grey deposit of arsenic, quite adherent and capable of withstanding scratch-brushing though lightened somewhat in the process. The work should be rinsed in hot water, quickly dried in hot sawdust, and lacquered. Many other recipes include the addition of copper and iron salts, the value of which is very doubtful.

Use of Platinum.—This metal being very electro-negative, is readily turned out from its salts by most of the metals, and uniform deposits can be obtained from dilute solutions in water or alcohol upon copper, brass, and silver. The deposit has the great advantage of permanence, but against this must be set the cost of the materials.

Very weak solutions of platinum chloride containing as

little as or even less than 5 parts of the chloride per thousand of water serve for this purpose. In such solutions brass, copper, and silver receive a light steel-grey to black deposit, the darker colour with the stronger solution. It is improved by greater uniformity by gently scratch-brushing. The deposit, however, becomes powdery by continued immersion.

Production of Coloured Films.—The following are a few striking examples :—

R.	Copper sulphate	25 grams
	Water	50 c.c.

The solution is used warm, and by the immersion of thoroughly cleaned specimens of copper a good light-brown colour on the pure metal is produced. In the same solution brass is turned a dark greenish-grey colour. The effect of impurities is thus most marked, and even with a sample of ordinary commercial copper the colour is considerably darker than that on the pure metal.

Parcel coppered brass work thus gives a satisfactory contrast.

These colours may not be obtained by a single immersion. If the first attempt is unsatisfactory the work should be thoroughly cleaned, and all traces of the colour removed before making a further attempt.

As the colours produced are oxides of copper, which are attacked by acid fumes in the atmosphere, the colours must be rendered more permanent by subsequent lacquering.

R.	Copper nitrate	20 grams
	Water	50 c.c.

This solution used warm gives most satisfactory results on both copper and brass. The colours are of greater contrast than those of the previous solution. Pure copper assumes a light chocolate brown colour. Brass is turned to a dark sage green, while various grades of commercial copper are coloured to different shades of brown passing almost to black. The

solution has a strongly oxidizing character, and the colours are due to oxides. As the chief oxide of copper is black, a good black colour can be produced on copper or brass by immersion in the solution, drying by warming without rinsing, and heating either well over a bare flame or on a hot stove. The nitrate is decomposed to oxide, and a good uniform black can be obtained by this method, by subsequently well brushing with a soft brush.

The addition of ammonia to these copper solutions makes a marked effect on the colours produced.

R.	Copper sulphate	25 grams
	Water	75 c.c.
	Strong ammonia solution	q.s. ¹

The copper sulphate solution is first prepared, and to it ammonia is added a little at a time with stirring. A green precipitate is first formed, and subsequently dissolves by the addition of more ammonia, forming a clear azure blue solution. *Excess of ammonia must be avoided.* An insufficiency is preferable to an excess, as the oxides of copper of which the colours are composed are soluble in ammonia, and if much of this reagent is present as an excess, no satisfactory effects can be obtained.

The solution when warmed has not a very marked effect upon copper, giving only a faint reddish tinge to it. On brass the colour is much darker than in the sulphate solution alone, and on parcelled work the two metals give a most satisfactory colour contrast. A still better effect, however, is obtained in the following solution :—

R.	Copper nitrate	20 grams
	Water	50 c.c.
	Ammonia	q.s.

The solution is prepared as before, and is of a deep blue

¹ "q.s.," in sufficient quantity.

colour. Excess of ammonia must be avoided. Pure copper takes a slight crimson colour in the warm solution, while brass receives a good black deposit. This may not be uniform by a single application, but a second or third immersion with due care cannot fail to produce satisfactory results, and yield a good black coloration. On parcelled work this provides a most striking contrast. The action is considerably slower in cold and weaker solutions, but where a quantity of small work is being done, a longer immersion in a weaker solution can be given, this demanding less attention.

In a similar manner many other compounds of copper lend themselves for use in these colouring processes, such as the acetate, chloride, and others. Further examples, however, must be sought in the text-book previously referred to.

Use of Sulphides.—The sulphides of the common metals are of various colours. Those of copper, lead, silver, and iron are black; that of tin is brown, and of zinc, white. Of these sulphides, those of copper and silver are of the greatest interest for the purpose of metal-colouring. They must be formed from more easily decomposed sulphides, especially those which are soluble in water. Sulphides available for this purpose are ammonium sulphide (Am_2S), of which the yellow liquid is an impure form though suitable for colouring purposes, potassium sulphide (K_2S), or liver of sulphur, barium sulphide (BaS), and sulphuretted hydrogen (H_2S).

By exposure to sulphuretted hydrogen, which comes off from each of the above sulphides by decomposition even by exposure to air, silver and copper at once begin to assume a series of coloured tarnishes, the colour depending upon the duration of the exposure. For ordinary purposes a quicker result is required. This may be obtained as follows:—

R.	Ammonium sulphide	1 volume
	Water	20 volumes

The mixture is dilute and inexpensive. In the cold, or more readily in the warm solution, copper suffers a series of

changes from light brown to dead black. The actual shade produced may be regulated with ease. The changes take place slowly in a cold dilute solution. At first the effect may be uneven, but greater uniformity is given by gently scratch-brushing. An extended immersion produces a black film, but by scratch-brushing this may be gradually reduced through dark brown to light brown, or even entirely removed. The method is capable of extensive application, and is much used, very artistic effects being produced on suitable work by sand-blasting the deeper portions, and burnishing the raised parts before submitting the work to the solution, and subsequently carefully relieving by light scratch-brushing. Brass is but little affected by the solution, but may first be coppered. All kinds of iron, steel, zinc, and other metal work can be similarly treated by coppering first in the cyanide bath.

R.	Barium sulphide	1 gram
	Water	100 C.C.

This solution has the same effect as ammonium sulphide, but is slower in its action, and is more suitable for colouring silver. In it, silver acquires almost every shade between a golden tint and bluish-black, according to the temperature and length of immersion, and the work may be varied by relieving, etc. Silver goods treated in this manner are said to be "oxidized." It will be readily understood that the stain produced by these sulphides is one of silver sulphide, and "sulphidizing" would therefore be a more correct term. The same compound is produced when silver goods are exposed to air, when an eggspoon becomes discoloured, and when silver nitrate is used in conjunction with sulphuretted hydrogen in rendering non-conducting materials conductive ready for deposition.

Metallochromes.—An interesting example of metal-colouring is seen in the production of thin films of lead peroxide on polished surfaces of iron or nickel. In most lead solutions, while deposition of the metal is proceeding at the

cathode, an insoluble anode of the metals nickel or iron, undergoes a striking change in colour. A thin film of lead peroxide is formed, and exhibits remarkable colour effects dependent upon the shape of the cathode. The effect was first observed by Nobili in 1826, who used a polished steel anode in a weak solution of lead acetate. With a wire cathode, the point of which was held close to the anode, a series of rings appeared on the anode directly opposite to the cathode, and these rings increased in diameter as the current was increased, or the deposition continued. The beautiful colours produced are due to the splitting up of the light by reflection from the gradually decreasing thickness of the film. Cathodes of different shapes may be used, and if held close to the anode, the shape of the anode effect is almost that of the cathode, and as the experiment is continued, the effect gradually passes off into a more or less rounded form. Other solutions of lead are equally effective, a good result being easily obtained from a solution of litharge in potash or soda.

CHAPTER XX

Qualitative Analysis.

Effect of Impurities in Metals and Solutions.—

Those who have experienced the trouble arising from the presence of a trace of copper in a nickel solution, or are aware of the change in colour of a gold deposit by the presence of copper or silver in the gilding solution, will at once understand the necessity for simple analytical methods as a means of tracing impurities in a solution, substance, or deposit. Further, when such impurities are discovered and identified, methods by which they may be removed will, if forthcoming, surely be welcome. It is the object of this section to indicate briefly the manner in which the commoner metals are chemically distinguished from each other, and, if needs be, separated from each other. Needless to say, this must be based on an intimate knowledge of the properties of the compounds of the metals, and their behaviour under the various conditions under which they are being used. Within the limits of one chapter it will be impossible to do more than briefly indicate the methods by which such analysis is conducted, and for a wider knowledge the student must be referred to the various text-books on qualitative analysis. The work involves accuracy and keen observation, as in many instances, a careless worker may entirely fail to observe a small quantity of an impurity, which, however, may be sufficient to exert a very detrimental effect in a solution.

Scope of Work.—In this section it is not intended to go beyond the usual methods of testing for the following metals:

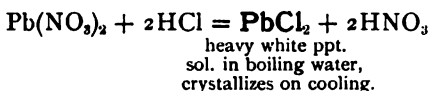
lead, silver, mercury, copper, tin, iron, aluminium, nickel, zinc, and manganese. It will be assumed that each of these may occur in a solution either alone or mixed with other metals. The problem is therefore to (1) identify the individual metals; (2) separate them; and (3) to do the analysis more thoroughly in order to determine the exact amount of each constituent.

Tests for the Metals separately.—In each case only the tests which are in most common use will be given. In each test it is assumed that the metal is in the form of a solution, and each test can be readily performed, and the results confirmed by simple test-tube experiment.

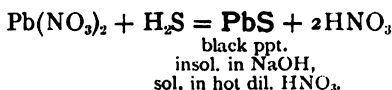
[NOTE.—The following abbreviations are frequently used: *sol.* for soluble; *insol.* for insoluble; *soln.* for solution; *dil.* for dilute; *str.* for strong; *conc.* for concentrated; *ppt.* for precipitate; *pptd.* for precipitated; *pptn.* for precipitation; *repptd.* for reprecipitated, etc.]

Lead.—Use a solution of lead nitrate $[\text{Pb}(\text{NO}_3)_2]$, or lead acetate $[\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2]$.

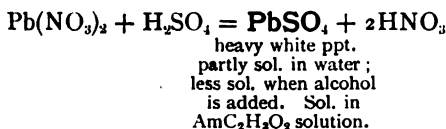
(1) Add dilute HCl.



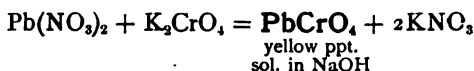
(2) Pass H_2S or add H_2S solution.



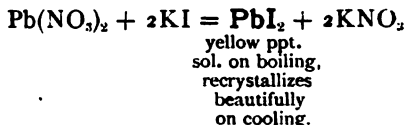
(3) Add dilute H_2SO_4 .



(4) Add K_2CrO_4 .



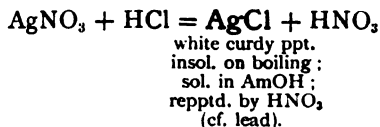
(5) Add KI.



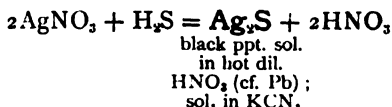
Of these five tests for lead some are very similar to those for other metals. For example, copper, silver, and mercury give black precipitates with H_2S . Silver gives a white precipitate with HCl . As these similar reactions are met, references will be made, in order that the results may be more carefully compared. Again, it will be obvious that by these similar reactions the metals may be divided off into groups or classes, while the characteristic tests will serve for the identification in, and separation of the individual metals from, these smaller groups.

Silver.—A solution of silver nitrate (AgNO_3) may be used.

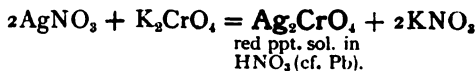
(1) Add HCl .



(2) Add H_2S solution or pass H_2S .



(3) Add K_2CrO_4 .



(4) Add Cu (turnings or thin sheet).



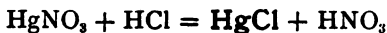
Mercury.—Mercury forms two classes of salts, viz.—

	Oxide.	Chloride.	Nitrate.	Sulphate.
(A) Mercurous.	Hg ₂ O	HgCl	HgNO ₃	Hg ₂ SO ₄
(B) Mercuric .	HgO	HgCl ₂	Hg(NO ₃) ₂	HgSO ₄

The two groups give different reactions.

(A) **Mercurous.**—Use mercurous nitrate (HgNO₃) dissolved in water with the aid of a little nitric acid.

Add HCl.

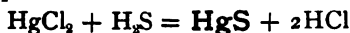


white ppt. insol.
in boiling water
(cf. Pb); insol.
but blackened by
ammonia (cf. Ag).

(B) **Mercuric.** — Use solution of mercuric nitrate [Hg(NO₃)₂] or mercuric chloride (HgCl₂).

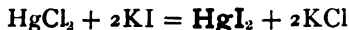
(1) Add HCl. No precipitate.

(2) Pass H₂S.



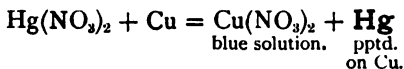
black ppt. insol.
in NaOH; insol. in
hot dil. HNO₃ (cf. Pb
and Ag); sol. in *aqua regia*.

(3) Add KI.



orange ppt.
sol. in excess KI
or HgCl₂ (cf. Pb).

(4) Add Cu.



To indicate the use to which these tests may be applied, it will be observed that the following separations are possible:—

Pb and Ag.—Precipitate with HCl. Boil mixed precipitates of PbCl₂ and AgCl with water. Filter while hot.

Pb and Hg(ous). Ditto.

Ag and Hg(ous). Precipitate with HCl. Treat mixed precipitate with AmOH. Filter.

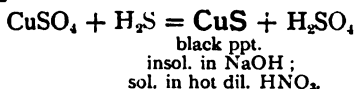
Ag and Hg(ic). Add HCl. Ag precipitated as AgCl. Hg(ic) remains in solution.

These are simple cases of analytical separations. Other combinations should also be made and the separations effected.

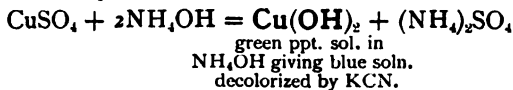
Copper.—Use a solution of copper sulphate (CuSO_4). The chloride, nitrate, or acetate would give the same results.

(1) Add HCl. No precipitate.

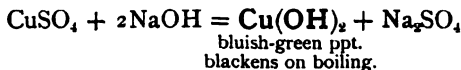
(2) Pass H_2S .



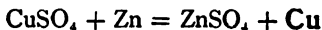
(3) Add NH_4OH .



(4) Add NaOH.



(5) Add Zn.

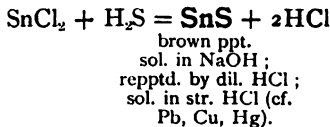


Suggestion.—Devise methods for separating Cu and Ag ; Cu and Pb ; Cu and Hg(ic) ; Pb, Ag, and Cu, etc.

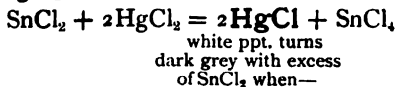
Tin.—Use solution of tin protochloride (stannous chloride, SnCl_2).

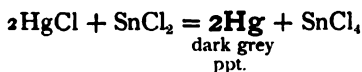
(1) Add HCl. No precipitate.

(2) Pass H_2S .



(3) Add HgCl_2 .





Hence copper and tin may be separated by precipitating both with H_2S , and treating precipitate with NaOH . Similarly, devise methods for separating Pb and Sn, Ag and Sn, etc., assuming that the metals are mixed in the soluble form.

The possible mixtures of the metals already dealt with are becoming more difficult, but as many mixtures as possible should be made and separated.

Separation of Pb, Ag, Hg(ous), Hg(ic), Cu, and Sn.

—Assuming that all these metals occur in a solution, and that it is required to separate them, we can, from the above reactions, draw up the method in Table XXVII. (p. 274).

It would seldom be necessary to deal with a solution containing all these metals, but the scheme is applicable for all ordinary mixtures of these metals. Examples of more possible occurrence will be given later.

Tests for Iron, Aluminium, Zinc, Nickel, and Manganese.

Iron forms two classes of compounds—ferrous and ferric. Some of the most important are tabulated as follows :—

	Ferrous.	Ferric.
Oxide . . .	FeO	Fe_2O_3
Hydrate . . .	$\text{Fe}(\text{OH})_2$	$\text{Fe}_2(\text{OH})_6$
Sulphide . . .	FeS	Fe_2S_3
Sulphate . . .	FeSO_4	$\text{Fe}_2(\text{SO}_4)_3$
Chloride . . .	FeCl_2	FeCl_3
Nitrate . . .	$\text{Fe}(\text{NO}_3)_2$	$\text{Fe}(\text{NO}_3)_3$
Phosphate . . .	$\text{Fe}_3(\text{PO}_4)_2$	FePO_4

Now, these two sets of salts behave almost as though they

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TABLE XXVII.

SEPARATION OF CONSTITUENTS OF A SOLUTION CONTAINING Ag, Pb, Hg(ous), Hg(ic), Cu, and Sn.

Add dil. HCl.¹ Cool.² Filter.³

Ppt. (PbCl ₂ , AgCl, HgCl). Wash. ⁵ Transfer to boiling tube. Boil with water. ⁶ Filter while hot. ⁷	Soln. (Hg(ic), Pb, Cu, Sn). Warm ¹¹ and pass H ₂ S ¹² till liquid smells strongly of the gas. ¹³ Filter.
Residue. NH ₄ OH through filter containing residue.	Soln. Cool. White crystalline ppt. ⁸ (PbCl ₂) or add K ₂ CrO ₄ . ⁹ Yellow ppt.
Residue. Black. Shows presence of Hg(ous).	Soln. ¹⁰ Acidify with dil. HNO ₃ . White ppt. AgCl. Shows presence of silver.
Residue. Black. Shows presence of Hg(ous).	Soln. Add H ₂ SO ₄ and alcohol. ²¹ Filter.
Residue. HgS. Dis-solve in <i>aqua regia</i> . Dilute solution. Add Cu. Bright deposit on Cu shows presence of Hg(ic).	Residue. (HgS, PbS, CuS, SnS). Warm with NaOH solution. ¹⁵ Dilute. ¹⁶ Filter. ¹⁷
Residue. HgS. Dis-solve in <i>aqua regia</i> . Dilute solution. Add Cu. Bright deposit on Cu shows presence of Hg(ic).	Soln. ¹⁸ Acidify with dil. HCl. Brown ppt. Shows presence of Tin.
Residue. HgS. Dis-solve in <i>aqua regia</i> . Dilute solution. Add Cu. Bright deposit on Cu shows presence of Hg(ic).	Ppt. White. Sol. in AmC ₂ H ₃ O ₂ . ²² Shows presence of Lead.
Residue. HgS. Dis-solve in <i>aqua regia</i> . Dilute solution. Add Cu. Bright deposit on Cu shows presence of Hg(ic).	Soln. Add AmOH. Green ppt. and blue solution. Shows presence of Copper.

Soln.¹⁴ All the metals having now been taken out, neglect this solution.

EXPLANATORY NOTES ON TABLE XXVII.

1. Dilute HCl precipitates Pb (though not completely), Ag, and Hg(ous), but *not* Cu, Hg(ic), and Sn.
2. PbCl₂ is less soluble in cold water, and hence cooling effects a more perfect precipitation.
3. Thus separating the precipitated AgCl, PbCl₂, and HgCl from the soluble Cu, Sn, and Hg(ic) compounds.
4. Lead occurs in this solution, owing to the slight solubility of PbCl₂ in water.
5. The precipitate, being still wet with the solution, contains small amounts of Cu, Sn, and Hg(ic). These are removed by washing. The washings may be added to the solution.
6. Because PbCl₂ is soluble in boiling water, while AgCl and HgCl are not.
7. To prevent recrystallization of PbCl₂.
8. Will only occur when Pb is present in appreciable quantity.
9. Make this test, even if no white crystalline precipitate is obtained.
10. Should contain the AgCl which is reprecipitated when the ammonia is neutralized.
11. Facilitates easy precipitation of the sulphides.
12. To precipitate Hg(ic), Pb, Cu, and Sn as sulphides.
13. Precipitation should then be complete.
14. If iron, nickel, or zinc had been present in the original solution, they would still remain in this liquid.
15. NaOH dissolves SnS, but not HgS, CuS, and PbS.
16. Otherwise warm strong NaOH would attack and destroy the filter-paper.
17. Hg, Cu, and Pb are now in the form of their sulphides on the filter paper.
18. Contains the tin.
19. As the precipitate is still wet with a solution containing tin.
20. Previous to adding alcohol, which would set up a violent reaction with the hot acid.
21. To make precipitation of PbSO₄ more complete.
22. Ammonium acetate. The solution can then be tested with K₂CrO₄ for lead.

were compounds of different metals. This will be clear from a comparison of the tests shown in Table XXVIII. (p. 276).

Perform these tests, using ferrous sulphate (green vitriol, FeSO₄·7H₂O), as typical of the ferrous compounds, and ferric chloride (perchloride of iron, FeCl₃) representing the ferric

TABLE XXVIII.
TESTS FOR IRON COMPOUNDS.

Reagent.	Ferrous compounds.	Ferric compounds.
1. Ammonium hydrate, NH_4OH	$\text{FeSO}_4 + 2\text{NH}_4\text{OH} = \text{Fe}(\text{OH})_2 + (\text{NH}_4)_2\text{SO}_4$ white ppt. quickly changing to light green, dark green, and finally to reddish-brown; thus— $2\text{Fe}(\text{OH})_2 + \text{O} + \text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3$	$\text{FeCl}_3 + 3\text{NH}_4\text{OH} = \text{Fe}(\text{OH})_3 + 3\text{NH}_4\text{Cl}$ Reddish-brown ppt. Sol. in dil. acid. Insol. in NaOH .
2. Sodium hydrate, NaOH	Ditto.	Ditto.
3. Sodium carbonate, Na_2CO_3	$\text{FeSO}_4 + \text{Na}_2\text{CO}_3 = \text{FeCO}_3 + \text{Na}_2\text{SO}_4$ white ppt.	$2\text{FeCl}_3 + 3\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} = 2\text{Fe}(\text{OH})_3 + 3\text{CO}_2 + 6\text{NaCl}$ Reddish-brown ppt. as above.
4. Potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$	Light blue ppt., darkening on exposure.	Dark blue ppt. (Prussian blue).
5. Potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$	Dark blue ppt. (Turnbull's blue).	Brown coloration.
6. Potassium sulphocyanide (thiocyanate), KCNS	No change.	Deep red coloration.

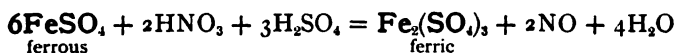
compounds. It often becomes necessary to identify a small amount of ferrous in the presence of a large quantity of ferric, and *vice versa*. For this purpose test 5 is most prominent for ferrous and test 6 for ferric. Further, there is always the tendency for ferrous compounds to slowly change to ferric, and hence in test 6 the ferrous compounds will frequently show a slight red coloration.

Interconversion of Ferrous and Ferric Compounds.—It is frequently necessary to convert the ferrous into ferric compounds, and *vice versa*. The former process is one of oxidation, and the latter, reduction.

Oxidation of Ferrous to Ferric.—The following reagents may be used: strong nitric acid (HNO_3), bromine water, sodium hypochlorite (NaClO), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and potassium permanganate (KMnO_4). In each case a little dilute H_2SO_4 should be added to the ferrous sulphate solution.

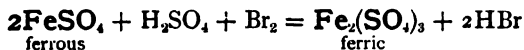
Using separate portions, and, after each experiment, testing the solution for ferric :—

(1) Add few drops of concentrated HNO_3 , and warm.

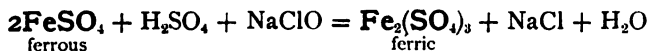


That this change has been effected will be readily observed by test 6 (p. 276).

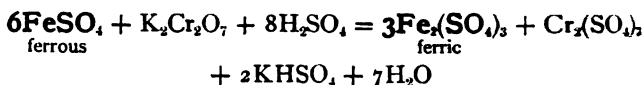
(2) Warm and add Br water until the colour of the Br is just permanent.



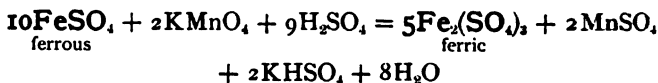
(3) Add a little NaClO solution.



(4) Add $\text{K}_2\text{Cr}_2\text{O}_7$ solution. A green colour is produced [$\text{Cr}_2(\text{SO}_4)_3$], but this is not sufficient to interfere with the ferric test.



(5) Add KMnO_4 solution. The persistence of the violet colour of the KMnO_4 marks the end of the reaction.

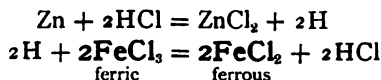


Methods (4) and (5) form the bases of quantitative methods of determining iron.

Reduction of Ferric to Ferrous.—The following reducing agents may be used: nascent hydrogen (produced by zinc in an acid solution), sulphuretted hydrogen (H_2S), sulphur dioxide (SO_2), and stannous chloride (SnCl_2).

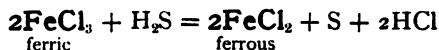
Using separate portions of ferric chloride solution :—

(1) Add zinc and HCl (dilute).



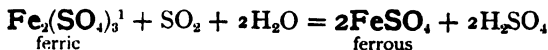
Test 5 (p. 276) may be used to show the presence of ferrous after this and subsequent tests.

(2) Pass H_2S gas.

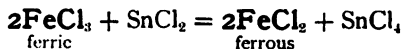


Test for ferrous either before or after filtering off precipitated sulphur.

(3) Pass SO_2 gas (sulphur dioxide).



(4) Add a little SnCl_2 solution.

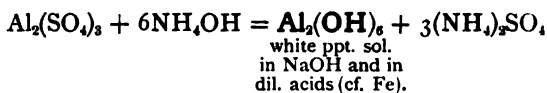


¹ $\text{Fe}_2(\text{SO}_4)_3$ taken in this equation for the sake of simplicity.

These oxidations and reductions are frequently required in analytical work.

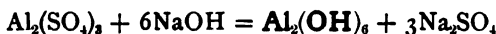
Aluminium.—Use a solution of either potash or ammonia alum, both of which contain $\text{Al}_2(\text{SO}_4)_3$.

(1) Add NH_4OH .

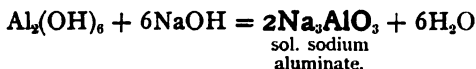


(2) Add NaOH.

(a) In small quantity.



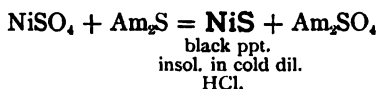
(b) In larger quantity.



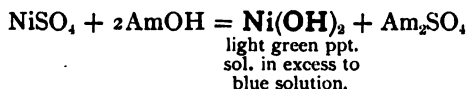
The solubility of $\text{Al}_2(\text{OH})_6$ in NaOH is accounted for by the production of this soluble sodium aluminate.

Nickel.—Use a solution of the sulphate (NiSO_4) or chloride (NiCl_2).

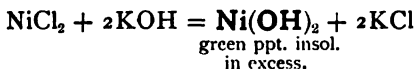
(1) Add ammonium sulphide (Am_2S).



(2) Add AmOH.

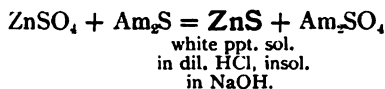


(3) Add NaOH or KOH.

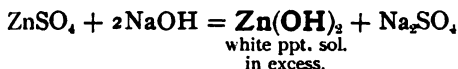


Zinc.—Use a solution of the sulphate (ZnSO_4), nitrate [$\text{Zn}(\text{NO}_3)_2$], or chloride (ZnCl_2).

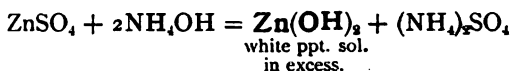
(1) Add Am_2S .



(2) Add NaOH.

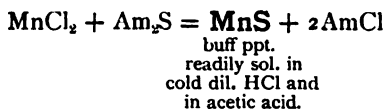


(3) Add NH_4OH .

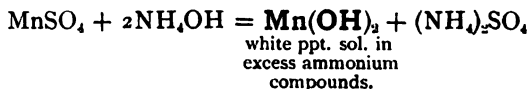


Manganese.—Use a solution of the sulphate (MnSO_4) or chloride (MnCl_2).

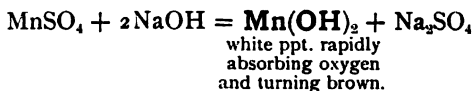
(1) Add Am_2S .



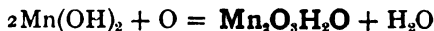
(2) Add NH_4OH .



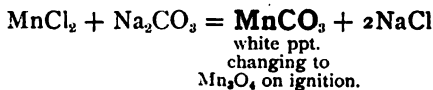
(3) Add NaOH.



The oxidation of Mn(OH)_2 produces—



(4) Add Na_2CO_3 .



Review of Tests for Fe, Al, Ni, Mn, and Zn.

Reviewing now the tests for iron, aluminium, zinc, nickel, and manganese, points of similarity and difference may be compared and summarized thus—

(1) None of these metals are precipitated by dilute HCl or by H_2S if the solution is acid. This at once suggests a method for separating them from Hg(ous), Ag, and Pb (which are precipitated with HCl), and from Cu, Hg, and Sn (which are precipitated by H_2S in acid solution).

(2) With ammonia, in the presence of excess of ammonium chloride, Al and Fe are precipitated as hydrates, while Zn, Mn, and Ni are soluble under same conditions.

(3) In a solution containing these five metals the iron and aluminium may thus be separated from the nickel, manganese and zinc by precipitation with ammonia.

(4) Then Ni, Mn, and Zn are precipitated by either Am_2S or by H_2S in an alkaline solution.

(5) Of the sulphides thus formed, viz. NiS (black), MnS, and ZnS, the Mn and Zn compounds are readily soluble in cold dilute HCl, while NiS is not. Hence separation of Ni.

(6) Mn and Zn differ in their behaviour with NaOH, both being precipitated, but the $Zn(OH)_2$ being subsequently redissolved.

Application of Foregoing Tests.—These principles may be applied in the following manner, which is preferably represented by a scheme similar to that drawn up for the previous metals. Imagine a solution to contain the five metals Fe, Al, Ni, Mn, and Zn. From this solution the metals may be separated by the method shown in Table XXIX. (p. 282).

Examination of a Solution for the whole of the Metals previously considered.—It will now be seen that the method for separating Fe, Al, Ni, Mn, and Zn can be at once applied to a solution from which Pb, Hg, Ag, Cu, and Sn have been removed, for the reagents used for removing the latter group of metals do not remove the former group from

TABLE XXIX.

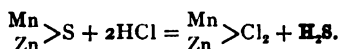
SEPARATION OF IRON, ALUMINIUM, NICKEL, MANGANESE, AND ZINC.

To solution containing these metals ¹ add a few drops of concentrated HNO_3 , and boil.² Cool.³ Add AmCl in excess ⁴ and AmOH in excess.⁵ Filter.⁶

Ppt. $[\text{Fe}_2(\text{OH})_6]$ and $\text{Al}_2(\text{OH})_6$. Wash. Reject washings. Dissolve ppt. in dil. HCl . ⁷ Add excess NaOH . Filter.	Soln. Add a few drops of litmus. Acidify, ⁹ with HCl . Add AmOH till alkaline. White ppt. Shows Presence of Aluminium.	Soln. Add Am_2S_3 , avoiding excess. ¹⁰ Filter.	Soln. Neglect.
Ppt. Reddish brown, $\text{Fe}_2(\text{OH})_6$. Dissolve in dil. HCl , and add $\text{K}_4\text{Fe}(\text{CN})_6$. Dark blue ppt. Shows Presence of Iron.	Residue. ¹² Black, NiS . Shows Presence of Nickel.	Ppt. Shake with cold dil. HCl . ¹¹ Filter.	
	Soln. Boil off H_2S . ¹³ Add NaOH ¹⁴ in excess. Filter.		
	Ppt. White, rapidly changing to brown. Shows Presence of Manganese.	Soln. Pass H_2S . White ppt. Shows Presence of Zinc.	

EXPLANATORY NOTES ON TABLE XXIX.

1. But not any of the metals previously mentioned in Table XXVII.
2. Converts ferrous into ferric compounds, ferric hydrate being much more easily precipitated and filtered.
3. Previous to adding ammonia.
4. Assists in preventing precipitation of nickel, manganese, and zinc with AmOH .
5. Precipitates $\text{Fe}_2(\text{OH})_6$ and $\text{Al}_2(\text{OH})_6$ even in presence of ammonium chloride.
6. Completing the separation of Fe and Al from Ni, Mn, and Zn.
7. May be dissolved by pouring warm dilute HCl through the paper containing the precipitate.
8. Solution contains the Ni, Mn, and Zn.
9. Alkali must be completely destroyed.
10. As excess of Am_2S redissolves NiS , giving a brown solution.
11. Not the ordinary dilute acid (which is about 1 to 3), but further diluted with twice its bulk of water.
12. This precipitate needs no confirmation if cobalt cannot be present.
13. H_2S formed thus—



If H_2S is not removed by boiling, then the addition of NaOH would bring about the reprecipitation of the two sulphides, and thus fail to effect separation.

14. Precipitates $\text{Mn}(\text{OH})_2$ (which turns brown) and $\text{Zn}(\text{OH})_2$ which redissolves in excess.

a solution. Without filling in all the details of the separation of each metal, Table XXX. (p. 284) shows the general scheme. Suppose a solution to contain all these metals; then—

(1) Dilute HCl precipitates Ag, Pb, and $\text{Hg}(\text{ous})$; after which—

(2) H_2S precipitates (from this acid solution) Pb, $\text{Hg}(\text{ic})$, Cu, and Sn; subsequently, after boiling off excess of H_2S —

(3) AmCl and AmOH may be used to precipitate Fe and Al, after which—

(4) Am_2S will precipitate Ni, Mn, and Zn.

TABLE XXX.

EXAMINATION OF A SOLUTION WHICH MAY CONTAIN Pb, Hg(ous), Ag, Hg(ic), Cu, Sn, Fe, Al, Ni, Mn, AND Zinc.

Add dilute HCl. Cool and filter.

Ppt. AgCl, PbCl ₂ , HgCl. Examine ppt. as shown in Table XXVII., on p. 274.	Soln. Warm ; pass H ₂ S until liquid smells strongly of the gas. ¹ Filter. ²		
Ppt. PbS, HgS, CuS, and SnS. Examine ppt. as shown in Table XXVII., on p. 274.	Soln. Boil off H ₂ S. ² Add a few drops conc. HNO ₃ . Cool. Add excess AmCl and AmOH. Filter.		
	Ppt. Fe ₂ (OH) ₆ , Al ₂ (OH) ₆ . Examine as in Table XXIX., on p. 282.	Soln. Pass H ₂ S or add Am ₂ S. Filter.	
		Ppt. NiS, MnS, and ZnS. Ex- amine as in Table XXIX., on p. 282.	Soln. Neglect.

The following notes on Table XXX. should also be carefully studied in addition to those already given for the two previous tables.

1. If previous to passing H₂S through the whole of the solution, the gas is passed through only a small portion, then in the absence of a precipitate there is no necessity to pass the gas through the whole solution, and the operation of boiling off the H₂S will be avoided.

2. Frequently a white precipitate is obtained. It is usually very fine, and may even pass through the filter paper. The precipitate may be filtered off as well as possible and neglected. Its formation is a sign of the presence of an oxidizing agent in the solution. (See reduction of ferric compounds with H₂S.)

3. Otherwise, on adding AmOH, Am₂S would be formed with the precipitation of Fe and Al as hydrates, together with Ni, Mn, and Zn as sulphides.

Seldom, however, would all these metals occur together, and it may therefore be well to indicate the course of an analysis in some possible case. For example, a solution

containing copper, iron, and nickel would, under this analytical scheme, behave as shown in Table XXXI.

TABLE XXXI.

GIVEN A SOLUTION FOR TESTING.

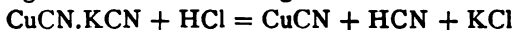
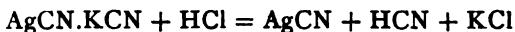
<p>Added ¹ dil. HCl. Cooled.</p> <p>Ppt. May be PbS, HgS, CuS, and SnS. Washed. Warmed with NaOH soln. Filtered.</p>	<p>No ppt.² Absence of Ag, Pb, and Hg(ous). Solution then warmed and passed H₂S. Black ppt.³ Filtered.</p> <p>Soln. Boiled off H₂S. Added a few drops conc. HNO₃. Boiled. Cooled. Added excess AmCl, and then AmOH. Filtered.</p>
<p>Residue. Washed. Warmed with dil. HNO₃. Completely dissolved.⁴</p> <p>Absence of Hg.</p> <p>Soln. Cooled. Added H₂SO₄ and alcohol. No ppt.</p> <p>Absence of Pb.</p> <p>Soln. Added AmOH in excess. Blue soln. Shows Presence of Copper.</p>	<p>Ppt. Red; therefore Fe present.⁵ Dissolved in dil. HCl. Added excess NaOH. Filtered.</p> <p>Ppt. Dis-solved in HCl. Added K₄Fe(CN)₆. Blue ppt. Shows Presence of Iron.</p> <p>Soln. Acidified with dil. HCl. Added excess AmOH. No ppt. Absence of Aluminium.</p>
	<p>Soln. Added Am₂S. Black ppt. Filtered.</p> <p>Ppt. Black⁶; therefore Ni present. Treated with cold dil. HCl. Filtered.</p> <p>Residue. Black. Presence of Nickel.</p> <p>Soln. Boiled off H₂S. Added excess NaOH. No ppt. Absence of Mn. Passed H₂S. No ppt. Absence of Zinc.</p>

Solution thus contains Copper, Iron, and Nickel.

NOTES ON TABLE XXXI.

1. Past tense used, representing work done.
2. Hence no necessity for filtering.
3. May contain brown tin sulphide (SnS), which must be tested for.
4. At this stage the precipitate may not completely dissolve, but leave a light yellow mass. This is sulphur, and may retain some of the black precipitates. Neglect this sulphur.
5. Red precipitate while proving Fe present does not prove absence of aluminium, and hence this metal must be tested for.
6. Precipitate being black definitely proves nickel to be present. Subsequent examination must be made to ascertain whether the precipitate contains ZnS or MnS.

Such, then, is the method by which solutions may be examined for the ordinary metals. Much, however, depends upon the original condition of the solution. Cyanide solutions, for instance, require rather special preliminary treatment. Take the case of a solution containing cyanide of silver and copper (AgCN.KCN) and (CuCN.KCN). On these compounds dilute HCl has the following action:—



and the single cyanides are precipitated.

Subsequent boiling with strong HCl converts these cyanides into chlorides, of which the copper compound is soluble, and silver chloride insoluble. The silver chloride can then be filtered off, and the solution contains copper, and can be subjected to the ordinary method of analysis. Similarly with a solution containing mercury cyanide, *e.g.* a quickening solution, by boiling with HCl the double cyanide is converted to soluble mercuric chloride, which will subsequently be precipitated with H_2S .

Treatment of Solid Compounds and Alloys.—

When the substance to be examined is a solid, it must first be dissolved.

A solution in water should be made if possible.

Failing this, try diluted HCl, cold or warm. If this is

unsuccessful, use hot strong HCl. In only very special cases would the substance now remain insoluble.

Cool the solution, dilute, and proceed with the analysis.

Metals and Alloys.—Of the metals treated above, only tin is insoluble¹ in strong HNO₃. The metal or alloy in the form of filings, shavings, or turnings is therefore treated with moderately strong HNO₃ until no further action ensues. Evaporate nearly to dryness, to expel excess of acid. Dilute. Filter if necessary.

Residue. White. Shows presence of tin.	Soln. Examine according to Table XXX., on p. 284, for all the metals except tin.
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¹ Aluminium when present in alloys dissolves readily in the acid, though some difficulty might be experienced in dissolving the metal alone.

CHAPTER XXI

Applications of Qualitative Analysis

Introduction.—The principles of qualitative analysis, briefly treated in the previous chapter, constitute the foundation of analytical work, and are important to the electroplater for many reasons. In the first place, one who uses chemical substances on even a moderate scale should have some idea of the composition, properties, and purity of the substances in use, and the reasons for which they are chosen for particular purposes. Secondly, some chemical substances in the course of their preparation may accumulate impurities which exert a harmful effect when the substances are applied. Thirdly, where precious metals are concerned it frequently becomes necessary to test for their presence before throwing away some otherwise waste material. Fourthly, common chemicals may even be adulterated. Simple analyses would in many cases serve to detect this. Hence this matter of analysis is an important one, and a few examples of tests which might become necessary are therefore given. These indicate, rather than give the exact details, the methods by which other similar problems may be tackled.

Test for Copper in a Silver Plating Bath.—Take a few c.c. of the solution and boil with about the same bulk of strong HCl. The silver is converted into insoluble AgCl, while copper (if present) forms soluble cupric chloride (CuCl_2). Filter. The solution, if copper is present in appreciable amount, is green. Copper, however, may be present in

too small a quantity to exhibit its colour. Test for it then by adding to the solution either—

(1) H_2S , forming a black precipitate, or

(2) $\text{K}_4\text{Fe}(\text{CN})_6$, giving a chocolate-brown precipitate very characteristic of copper.

In the H_2S test a very small amount of copper produces only a brown coloration, which, on standing, may separate out as a fine precipitate. Other metals like lead, mercury, and tin, would, if present, interfere with this test, and the black precipitate produced with H_2S should be examined for these metals as shown in Table XXVII. on p. 274. The delicacy of the test for copper may be shown by taking about 100 c.c. of a solution containing only 1 milligram ($=0.001$ gram) of copper, and passing H_2S . A decided brown colour is formed which, on standing, yields a fine black precipitate.

It should be added that the presence of copper in a silver-plating solution involves no great danger of the deposition of that metal with the silver. The author has shown¹ conclusively that even when copper is present in a large preponderance, the silver deposit contains barely a trace of the impurity. Of much more importance is the matter of keeping the nickel solution free from copper.

Testing Nickel Solutions for Copper.—Take about 20 c.c. of the bath, acidify with dilute HCl , warm, and pass H_2S . If copper is present a black precipitate is produced. Lead, mercury, silver, and tin would give the same results, but none of these are likely impurities. From a nickel solution containing only the smallest amount of copper, a black deposit is obtained, and in a plating shop where copper sulphate is so much used, small amounts of copper will find their way into the bath unless much care is exercised. When this happens the anodes become red, due to deposition by simple immersion. The point is one of some considerable importance, as a simple and slight accident may completely damage a large volume of solution. Thus, if a 200-gallon vat contains

¹ *Trans. Faraday Soc.*, vol. vi. 1910, p. 5.

12 ozs. of double salts per gallon, the total quantity of double salts is 150 lbs., which at 4d. per lb. is worth 50s. Some effort, therefore, might be made to avoid this waste by the removal of the copper. To effect this, a number of methods based on simple analytical work might be suggested. Thus the copper might be removed by—

(1) Acidifying, passing sulphuretted hydrogen, allowing precipitate to settle, decanting off clear liquid (neglecting the precipitate), getting rid of excess of H_2S by blowing steam through the solution, and finally neutralizing the acid with ammonia. On a small scale, for experimental or analytical work, the removal of the copper is most complete, but such a tedious method would be impracticable on a large tank of liquid. Or—

(2) Acidifying, and by slow deposition, using either nickel anodes or platinum, practically the whole of the copper can be deposited. This again is sufficiently complete for experimental work, but on a 200-gallon solution it could hardly be expected to justify the time. A considerable amount of acid would be required, and at the end of the deposition of copper it would need neutralizing. Much of this might be done with nickel carbonate, thus increasing the nickel content of the solution, and finally neutralizing with ammonia.

The only alternative, therefore, is the method of recovering a large proportion of the double nickel salts by the addition of ammonium sulphate, sacrificing some of the nickel in the waste solution, which also contains the copper.

Iron in Copper Sulphate.—This is a likely impurity, though not a dangerous one. To examine for it, take a few grams of the bluestone and dissolve in water, or about 20 c.c. of the solution if this has to be tested. The copper must now be entirely removed, and this is done by slightly acidifying and passing H_2S . Filter off the precipitate, and pass the gas again through the filtrate to ensure complete precipitation. Filter again if necessary. Boil off H_2S from the filtrate, and when the gas is expelled add a few drops of strong HNO_3 and boil

again. Cool and add excess of ammonium hydrate. A slight reddish-brown precipitate (which in any case cannot be large) indicates iron. In an ordinary acid bath, this would not be at all injurious, for at quite ordinary current densities it remains in the solution when so much acid is present. The method indicated above is one which is capable of slight modification to make the test quantitative. Other methods by which the test may be made are—

(1) Getting rid of the copper by H_2S as already described, and, after boiling off H_2S and oxidizing with HNO_3 , add—

(a) Potassium sulphocyanide, when iron is indicated by a deep red coloration.

(b) Potassium ferrocyanide, when iron is indicated by a dark blue precipitate.

(2) To the original solution add ammonia in excess. The copper is precipitated and redissolved, while the iron is precipitated but not soluble in excess. By filtering and washing, it would be recognized by its colour.

Testing Nickel Salts for Iron.—Iron is a possible impurity in nickel salts. Examine for it as follows :—

Dissolve a small quantity in water. Add ammonium chloride and ammonia in excess. If the nickel is precipitated it is dissolved by the excess of ammonia, the iron remaining insoluble. Filter, and on washing away the blue colour due to the ammonio-nickel solution, the iron precipitate would be recognized. Its quantity would be small, and a more decided test can now be made upon it by dissolving it in dilute HCl and testing with potassium sulphocyanide, when the characteristic red colour would be more readily observed than would be the case in the presence of a large amount of nickel compound. The nickel salts of commerce are now much purer than they were a few years ago, and iron is seldom present in even small quantities.

Analysis of Metals and Deposits.—If a solution is required pure, it is obvious that impurities must be avoided in the anodes. Simple tests may be used in most cases.

Copper in Silver Anode.—Silver anodes should be of fine silver, and not contain copper. Though it is safe to buy new anodes of fine metal, it may still happen that in some works, scrap will require testing to ascertain its suitability for small anodes or for making up a fresh solution. Dissolve a small portion in moderately strong nitric acid. Pure silver dissolves, forming a colourless solution, while the presence of copper is indicated by a green colour, and the extent of this colour gives a rough idea of the amount of copper present. If only a very faint colour is produced, evaporate off the acid, dilute, add dilute HCl to precipitate the silver as chloride, and filter. Copper may now be tested for by the methods already described. Silver containing an appreciable amount of copper might be worked up to a plating solution free from copper by dissolving the metal in nitric acid, precipitating the silver as chloride, and after washing the chloride, dissolving it in cyanide. No separation would be effected by using cyanide to precipitate the silver, as copper goes through the same course of reactions.

Testing Deposits.—In the course of any investigation on the deposition of an alloy, frequent tests would need to be made in order to ascertain whether the several metals are present. The mere colour would not be wholly indicative. Thus in depositing German silver, a white deposit might be obtained containing much zinc and nickel with or without copper, or a white alloy might be obtained containing copper and nickel with or without zinc. Hence analysis becomes necessary, especially to discover traces which may not profoundly modify the colour. The following are examples :—

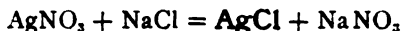
Testing a Copper Deposit for Zinc.—It is obviously desirable to produce such deposits upon a metal from which the deposit may subsequently be dissolved. Platinum is very convenient for this purpose, and cathodes of the sheet metal or gauze mounted on a rigid wire frame are in common use. From such a cathode practically the whole of the metals may

be removed by a single acid, the notable exception being gold, which, moreover, could not be removed by means of *aqua regia*, as this acid would also dissolve the platinum, but could be removed by making it the anode in a weak cyanide solution. From such a platinum cathode, a copper deposit is removed by immersing in warm dilute HNO_3 . After removing the cathode and rinsing it, the liquid is evaporated to expel excess of acid, diluted, and saturated with H_2S to remove the copper. Zinc cannot be tested for in the presence of copper, for this metal interferes with all the zinc tests, and so a small amount of zinc may hide away in a large amount of copper. By first removing the copper the zinc may then be tested for. The separation of the copper should be complete, as any trace remaining interferes with the zinc test. If the clear filtrate still containing H_2S is now made alkaline with ammonia or caustic soda, zinc, if present, is indicated by a white precipitate. If nickel is present a black precipitate appears at this stage, but this is a most unlikely impurity in deposits of brass.

Testing a Copper Deposit for Tin.—In making preliminary experiments in the deposition of bronze it may be necessary to examine some deposits in order to ascertain whether tin has actually been deposited. The deposit is removed by nitric acid, when copper is dissolved and tin is converted to a loose insoluble oxide. If this is carefully done in an evaporating dish and the cathode washed with distilled water, the tin should be observed as a deposit at the bottom of the dish. No further test would be required, and for a quantitative experiment this white tin oxide is collected, washed, dried, and weighed.

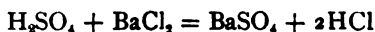
Testing Nitric Acid for Chlorides.—Nitric acid to be used for dissolving silver should be free from hydrochloric acid or chlorides. If these are present in the acid, silver chloride is formed as an insoluble compound when the metal is dissolved. Hence the necessity of pure acid for the purpose. Dilute a few c.c. of the acid with water. Add a few drops of

silver nitrate solution. A turbidity or precipitate indicates the presence of chlorides thus—



If only a faint milkiness is produced, the amount of this impurity is practically negligible, but a perceptible precipitate should not be obtained. The presence of hydrochloric acid arises probably from the presence of chlorides in the original materials (Chili saltpetre and oil of vitriol) from which the acid is made. For ordinary dipping acid small amounts of hydrochloric acid would not be at all harmful.

Testing Acids and Liquids for Sulphuric Acid and Sulphates.—The presence of sulphuric acid or soluble sulphates is readily shown by the addition of dilute hydrochloric acid and barium chloride (BaCl_2), when a white precipitate of barium sulphate is formed.



Barium sulphate is remarkable for its great insolubility, and the smallest quantities are therefore easily observed, and the test is a delicate one. The addition of hydrochloric acid is very essential, and if any action occurs by this addition, such as the decomposition of a carbonate with the evolution of carbonic acid gas, the acid must be added until no further action occurs. Hydrochloric acid is added to prevent other similar reactions from taking place. Thus if barium chloride is added to a sodium carbonate solution, a white precipitate would be produced, but this would be entirely soluble in hydrochloric acid, and its formation is prevented by the presence of that acid.

Further, the barium chloride test does not necessarily prove the presence of free sulphuric acid in a copper sulphate bath, for copper sulphate produces the same result as the acid. Hence, in the absence of other acids, free sulphuric acid would have to be tested for by litmus (which is unsatisfactory

in the presence of many metallic salts), or preferably by the addition of an alkali. In the absence of acid, caustic soda produces an immediate precipitate with copper sulphate. If acid is present an appreciable amount of alkali (depending upon the amount of free acid present) would have to be added before a permanent precipitate could be obtained.

Numerous other examples of interest and workshop importance might be mentioned and described in detail. The foregoing, however, may serve as types, and if these simple principles are understood and their importance fully appreciated, the student will be able to turn his attention to treatises dealing more particularly with this phase of applied chemistry.

CHAPTER XXII

Quantitative Analysis

Introduction.—Having now some idea of the methods by which solutions, deposits, metals, or materials can be analyzed to ascertain the nature of their constituents, further steps can be taken in order to determine the actual quantities in which such constituents occur. This is the idea of **Quantitative Analysis**, and a considerable amount of quantitative work can be carried out with quite simple apparatus and in a simple manner. From the electroplater's point of view, quantitative analysis can be applied in many directions, in the examination of materials, solutions, dips, deposits, stripping liquids, and residues. Nor must it be considered that analytical methods are superfluous. All phases of applied chemistry, especially those of commercial importance, need to be rigidly observed by such quantitative methods. In what follows in this and succeeding chapters, it is not intended to give detailed methods by which analyses are carried out. Principles particularly are aimed at, together with a brief account of the special apparatus used and methods applied.

While quantitative analysis can only be pursued with accuracy after some experience, still there is much analytical work which can be carried out with approximate results, and should therefore be applied in the workshop, by means of cheap apparatus. It is hoped, however, that an outline of such methods may prove an incentive to many to make frequent use of the methods suggested, and by extending their

application, gradually replace rule of thumb methods by those in accordance with scientific principles.

Methods of Quantitative Analysis.—The various methods by which quantitative analyses are conducted may be grouped as follows :—

Gravimetric, meaning those methods in which the substance is either actually obtained and weighed, or in which it is converted into a compound which is obtained and weighed. In either case the chief method of measurement is that of weighing. Such methods are of great accuracy if carried out with care.

Volumetric Methods are those in which most of the measuring is done by means of solutions of definite strength, measured volumes being added to bring about desired results. Here, again, the solutions of definite strength have to be prepared, usually by first weighing the substance which they contain, but weighings are reduced to a minimum. The accuracy of these methods depends very much upon the accuracy with which the measuring instruments are graduated. The solutions used are called **Standard Solutions**, and much depends upon the accuracy with which they are made up, and the purity of the materials employed.

The Balance.—A balance of some accuracy is an essential for all quantitative work. It is the most expensive piece of apparatus required, and on its accuracy and careful use much depends. For special analytical work, one costing £10 to £20 is essential, but for the more ordinary work described in succeeding chapters, an outlay of about £5 should secure one of sufficient accuracy. From the accompanying diagram (Fig. 108) it will be seen to consist of a rigid beam which swings on an agate knife-edge resting on a small flat agate plate. This supporting knife-edge is of great importance. The pans of the balance rest from the beam by similar knife-edges of agate attached in an opposite direction. Agate is very hard, and can be beautifully smoothed, and does not corrode with acid fumes. Steel knife-edges, which are put

on cheaper balances, are corroded by chemical fumes, and become sluggish in their action, thereby considerably diminishing the sensitiveness of the balance. When not in use, the beam of the balance rests on a support so that the knife-edges are just lifted from the agate planes or grooves. This is done to preserve them. In the process of weighing, the beam has

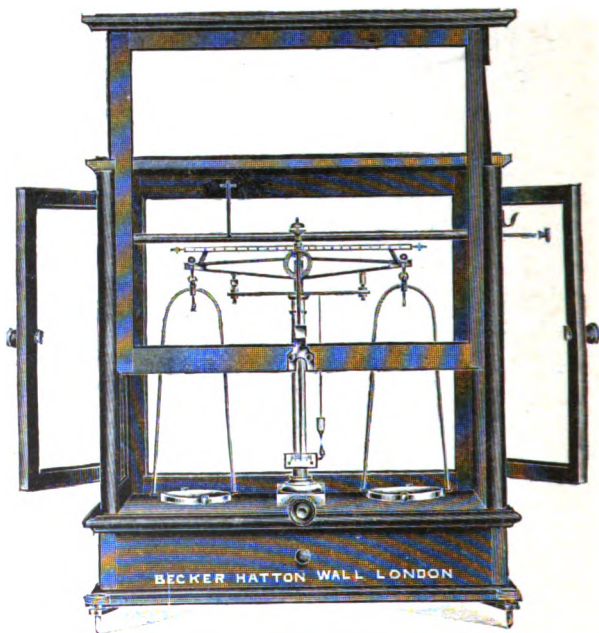


FIG. 108.—Chemical balance.

therefore to be raised from this support, and this is conveniently done by simple mechanism actuated from a small lever or milled screw at the front of the balance.

The weights invariably used are of the decimal or metric type, the **gramme** being the unit (Fig. 109). These are made to range usually from 100 to 1 gramme. Decimal parts are made of sheet metal, with one corner bent up so that they may be easily lifted by means of forceps. Such weights are

usually in the order of 0.5, 0.2, 0.1, 0.1, 0.05, 0.02, 0.01, and 0.01 gramme. Smaller weights are inconveniently small, and the readings in the third place of decimals are obtained by a small wire "rider." This weighs 0.01 gramme when placed in the pan or on the beam at a point immediately above the point of suspension of the pan. At other positions on the beam its effect is varied according to its distance from the centre of the beam. Each side of the beam is therefore graduated into ten equal parts, which are numbered, and according to the division on which it is placed the rider represents 0.001, 0.002 gramme, etc. Its position is readily altered by an arm and hook of convenient shape running over the beam. The balance is best contained in a case, the doors of which should be kept shut during the final stage of weighing and when the balance is not in use.

Rules for Weighing.—(1) In all except a few special cases, substances should not be weighed directly on the pan, but placed in counterpoised watch-glasses or other convenient receptacles.

(2) The balance should be carefully adjusted before weighing, so that its pointer moves to an equal number of divisions on either side of the scale.

(3) The substance to be weighed should be placed on the left-hand pan of the balance, and the weights on the right-hand pan.

(4) No change in the weights should be made until the beam is lowered on to its supports.

(5) Weights should be used in the order in which they occur in the box.

(6) When the smallest weight has been used, and an exact balance is not yet obtained, the rider is lowered on to the beam, and its position altered until correct.

(7) Volatile substances, or those which absorb or lose moisture, must be weighed in stoppered bottles or tubes.

(8) No weighing should be made with a substance which is at a different temperature from the air.

(9) The weight of the body or substance weighed is read from the weights absent from the box, and may be checked when the weights are replaced. The utmost care should be taken to accurately record all weights, as an error may entirely spoil a whole series of analyses.

Principles of Gravimetric Analysis.—The substance for analysis is taken in weighed quantity, and by chemical



FIG. 109.—Gramme weights.

methods special to each case is converted into a compound which (1) can easily be obtained in a pure form and weighed, and (2) is of definite and known composition. This compound is usually obtained as a precipitate, so that all other substances present shall remain in the solution. It is obtained by filtering, and purified from the liquid it retains by continued washing. It is then obtained quite dry by somewhat slowly drying in an air or water oven, and subsequently by igniting

it at a temperature sufficiently high to ensure complete expulsion of water, but not sufficient to cause the decomposition of the substance.

Precipitation.—Methods must now be selected which involve the precipitation of the substance to be estimated free from impurities, and it is at this stage that the knowledge of the principles of qualitative analysis are applied. For the common metals the following methods are adopted :—

Silver.—Precipitated as chloride by HCl . No other metal interferes except lead and mercury(ous), and these would not be present as a rule.

Copper.—(1) Precipitated by NaOH and weighed as CuO .

(2) Precipitated by H_2S in acid solution and weighed as Cu_2S .

(3) Precipitated with potassium thiocyanate (KCNS) and sodium bisulphite (NaHSO_3) and weighed as Cu_2S .

Method 1 would only be applicable in the absence of many other metals, and could as a rule only be applied on a pure salt or solution of copper. Method 2 would serve to separate copper from iron, zinc, nickel, and aluminium, but not from lead, tin, and silver. Method 3 is of wide application.

Iron.—Most usually converted to ferric, precipitated as $\text{Fe}_2(\text{OH})_6$ with ammonia, and ignited to Fe_2O_3 . This method can best be applied in the absence of other metals, as copper, lead, silver, aluminium, nickel, etc.

Aluminium, by a method similar to that of iron, weighing as Al_2O_3 .

Zinc, from a pure solution by precipitating zinc carbonate and subsequently igniting to oxide.

Nickel, by precipitating with NaOH and igniting to oxide (NiO).

Quantitative Separations.—In many other cases where two or more metals are present, the problem becomes more complex, for some of the metals present may first need to be completely separated without interfering with the one under estimation, and this may then have to be completely

precipitated free from other metals remaining in the solution. The qualitative methods outlined in the previous chapter cannot always be strictly followed in quantitative work, and special cases call for special methods.

The details of each stage cannot here be dealt with, but one or two special precautions in connection with the ignition of precipitates must be touched upon.

Ignition of Precipitates.—The final drying of a precipitate in readiness for weighing needs some care. Precipitates which are not stable at any elevated temperature must be dried with special care. They are usually dealt with on a **tared** filter paper. Two papers are separately folded into quarters (Fig. 110). A hole of about one inch in diameter is cut in the centre of the first paper, and from the

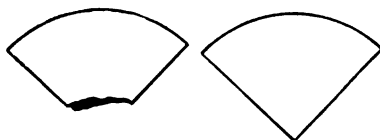


FIG. 110.—Tared filter.

edges of the second, sufficient paper is trimmed, till both papers weigh exactly the same. The two papers are then put together with the second inside the first, and they are placed in the funnel and the precipitate filtered and washed. After prolonged drying at $105-110^{\circ}\text{C.}$, they are allowed to cool, and then weighed, the outside paper being placed on the right-hand pan and the paper containing the precipitate on the left-hand pan. The weights now added to produce a balance show at once the weight of the precipitate. If in the process one filter paper suffers any loss by the acids or other liquids passing through it, or should retain a slight amount of moisture, it may be safely assumed that a similar change has occurred to the other, and these changes balance one another. When a precipitate may be ignited at a high temperature, or where a

high temperature is necessary to ensure that the compound is of definite composition, another method is usually followed. The precipitate is transferred as completely as possible to a weighed porcelain crucible. The paper is then folded as shown in Fig. 111, and held by a platinum wire wound round it, over the inverted crucible lid, and burned, allowing the ash to fall upon the lid. It can be further heated until the whole of the carbonaceous matter is burnt off. In burning the paper to ash the small amount of precipitate which remains on the paper may be reduced by the carbon of the paper, and adding this ash directly to the precipitate would give a mixture of indefinite composition. This is avoided by burning the paper separately and treating the ash in order that the reduced precipitate may be reconverted to its original composition.

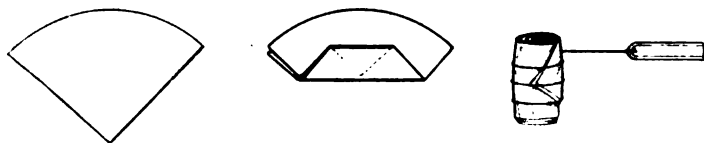


FIG. 111.—Filter paper folded for burning.

When this has been done, the lid is placed on the crucible and the precipitate ignited if necessary.

Volumetric Methods.—Volumetric analysis is conducted with solutions of definite strength called standard solutions. By the use of such solutions analyses can be carried out rapidly, though they may lack a little in accuracy. Thus if 10 grams of a substance are dissolved and the solution made up to 1000 c.c., then, after shaking, every 100 c.c. of the solution contain 1 gram, and every 25 c.c. contain 0.25 gram, and so on, and thus a large number of small amounts of the substance may be taken without the necessity of weighing them individually. The accuracy with which they are taken will depend to a large extent upon the accuracy of the weight of the original substance and that of the measures by which

the smaller quantities are withdrawn. Special apparatus is therefore made for this work, and usually graduated for exact volumes.



FIG. 112.—Measuring flask.

Measuring Flasks (Fig. 112) are made to contain 1 litre, 500 c.c., or 250 c.c., or other volumes, and are provided with a long narrow neck with a ground-glass stopper. A circular mark on the neck shows the level of the liquid when the flask *contains* the volume specified, usually at 15° C. They are used chiefly for making up liquids to a definite bulk.

Graduated Cylinders (Fig. 113) are used for a similar purpose, and while the flasks have only one mark, the cylinders may be graduated throughout their entire length, and so can be used for making up different volumes.

Against this, however, must be set the fact that graduations on a wide cylinder are not so accurate as that on the narrower neck of a flask. From the graduated cylinders, volumes of liquids can be poured and approximately measured.

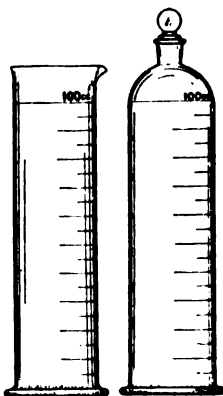


FIG. 113.—Measuring cylinders.

For transferring liquids in measured quantities, **pipettes** are used (Fig. 114). They are made to *deliver* given volumes of liquids—25 c.c., 50 c.c., etc. The liquid is drawn into them by suction with the mouth from above, and is held in them by rapidly placing the finger or thumb over the end, as shown in the diagram. The stem above the bulb carries a mark. If liquid is adjusted to this level, and this can be done by momentarily removing the thumb or finger, then on delivering the liquid, the whole of the

liquid is not discharged, but the volume discharged is that marked on the pipette. Thus a 25 c.c. pipette holds up to its mark more than 25 c.c., but delivers exactly 25 c.c. If pipettes are being used to transfer quantities of solution of definite strength, they should first be rinsed with that liquid. A little thought will show the necessity for this. If the inside of the pipette is wet with water, then as the solution enters the pipette it is diluted and its strength altered to an unknown extent. This can be obviated by rinsing the pipette first with a small quantity of the liquid, which is then thrown away. A pipette has but one mark and delivers but one volume of liquid.

Burettes (Fig. 115) are constructed to accurately deliver different volumes. They consist of accurately graduated tubes terminating in well-fitting stopcocks, and are capable of delivering up to 25, 50, or 100 c.c. of liquid, the graduations reading downwards. After thoroughly cleaning with water, they should be rinsed with the solution with which they are to be filled. The solution is then added till its level is above the zero mark, and is run out by means of the stopcock until the level stands at zero. If graduated, as is usual, in tenths of a c.c., the volume of liquid discharged can be easily read to 0.05 c.c. The value of the different pieces of apparatus will be gathered from the following example.

If 5 grammes of silver nitrate are dissolved and made up to 1000 c.c. in the flask, every 25 c.c. of the solution withdrawn (using a pipette) would contain $\frac{25}{1000} \times \frac{5}{1} = 0.125$ gramme AgNO_3 . If the solution is used from a burette, and 12.2 c.c. are delivered, then the amount of silver nitrate contained in this volume is $\frac{12.2}{1000} \times \frac{5}{1} = 0.061$ gramme.

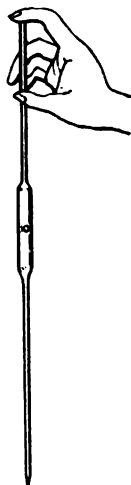


FIG. 114.

Standard Solutions.—A standard solution is one of definite strength used for comparing the strengths of other solutions. It is often possible to do this without knowing exactly the strength of the standard, in the same way that two lengths might be compared without knowing exactly the length of the unit taken as the means of comparison.



FIG. 115.—
Burette.

For most analytical work they are made to contain either a gram-equivalent,¹ or a definite proportion of a gram-equivalent of the substance per litre. Thus, when a gram-equivalent is contained *in* one litre, the solution is said to be **Normal** or **Equivalent**, and is denoted by N or E. Similarly, solutions containing—

One-half of a gram-equivalent per litre are **semi-normal**,

and are denoted $\frac{N}{2}$ or $\frac{E}{2}$

One-tenth of a gram-equivalent per litre are **deci-normal**,

and are denoted $\frac{N}{10}$ or $\frac{E}{10}$

One of the great advantages attached to such solutions is the fact that if they react with each other, exactly equal volumes of solutions of the same equivalent strength will be required to complete the reaction. Thus—

50 c.c. N . H_2SO_4 exactly neutralize 50 c.c. N . NaOH
and

25 c.c. $\frac{N}{10}$ HCl exactly precipitate 25 c.c. $\frac{N}{10}$ $AgNO_3$

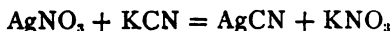
The strength (grams per litre) of some common volumetric solutions are given in Table XXXII.

¹ The chemical equivalent in grams.

TABLE XXXII.
STRENGTH OF STANDARD SOLUTIONS.

Solution.	N	$\frac{N}{2}$	$\frac{N}{10}$	$\frac{N}{100}$
Sulphuric acid . . .	49	24.5	4.9	0.49
Nitric acid . . .	63	31.5	6.3	0.63
Sodium hydrate . . .	40	20.0	4.0	0.40
Sodium carbonate . . .	53	26.5	5.3	0.53
Silver nitrate . . .	170	85.0	17.0	1.70
Potassium cyanide . . .	65	32.5	6.5	0.65
Iodine . . .	127	63.5	12.7	1.27
Sodium chloride . . .	58.5	29.25	5.85	0.585

One point of importance must be observed. From the present point of view the equivalent of the substance must be determined from the **reaction** into which the substance enters. An example will make this clear. Potassium cyanide precipitates silver nitrate as follows :—



when $170 \equiv 65$

This reaction is not used analytically owing to the great difficulty which is experienced in determining when the action is just completed. Again, when silver nitrate is added to potassium cyanide the following reaction occurs :—



when $170 \equiv 130$

If, therefore, silver nitrate is used to determine free cyanide in a solution, then up to the point of the first permanent precipitate, every 170 grams of AgNO_3 added have fixed 130 grams of KCN, while when KCN is added to AgNO_3 65 grams of KCN are sufficient to fix and precipitate the silver from 170 grams of silver nitrate.

An exactly normal or deci-normal solution requires great care in preparation, and as a rule is not absolutely necessary,

though most convenient when much work is being done. Other standard solutions in which the quantities of substances are not exactly equivalent but are nevertheless no less definite may be more easily made, and are all that is necessary for most ordinary work.

When prepared, standard solutions should be transferred to dry stoppered bottles and carefully labelled. In order to save the trouble of drying the bottle inside it may be rinsed out at least twice with small amounts of the solution before the bulk of the solution is added.

Standardization of Solutions.—For a solution to be prepared of any accurately known strength, pure materials only can be used. These, however, may not be at hand. It would be a difficult matter to weigh out exactly 4.9 grams of absolutely pure sulphuric acid. There would be some difficulty first in obtaining the acid absolutely pure. Again, potassium cyanide, though pure from a commercial point of view, could not be easily obtained of sufficient purity for analytical purposes. Yet these solutions are frequently required for ordinary analytical work. They are therefore made of approximate strength first, and their exact strength is ascertained by comparing them with some solution which can be accurately prepared from pure materials. This comparison is called **Standardization**. It amounts to this. A number of measurements have to be made, but a rule cannot be obtained for the whole of the time required for the measurements. A rod of indefinite length is therefore taken, and after determining its length by comparison with the rule, it can be subsequently used as a rule. Similarly with sulphuric acid: a solution of only approximate strength is first made up. Its exact strength is then found by comparing it with a carefully prepared solution of sodium carbonate, after which the acid, thus standardized, may be used to determine the strength of other alkali solutions. In a similar manner the following standardization processes are frequently resorted to—

Solution to be standardized.	Accurately prepared solution used.
HCl, HNO ₃ , H ₂ SO ₄ .	Na ₂ CO ₃ .
NaOH.	Previously standardized acid solution.
Sodium thiosulphate, Na ₂ S ₂ O ₃ .	Iodine.
KCN for copper estimations.	Solution of ammonio copper sulphate or nitrate.

In such cases the greatest care must be taken in the preparation of the original standard solution, as if this is inaccurate, all others standardized by it will be unreliable. Further, such standard solutions do not keep indefinitely. They may change slightly in composition, and hence will require re-standardizing at intervals.

End Reactions.—In adding a standard solution to bring about a given reaction, some means must be devised for determining exactly the point at which the reaction is just completed. This may be accomplished probably by a decided change of colour, or by the appearance of a permanent turbidity or precipitate. If such decided changes cannot be observed, substances must be added to the solutions so that when the standard solution is present in the slightest excess, an easily observed change will occur. Such substances are termed **indicators**. For example, in neutralizing acids and alkalis the presence of methyl orange at once shows the presence of one or the other in the slightest excess by a yellow colour with alkalis and a pink colour with acids. Phenolphthalein gives a still greater contrast, showing an intense violet colour with alkali which entirely and suddenly disappears with the presence of the smallest excess of acid. Such colour changes, however, could not be easily identified in the presence of other coloured compounds such as copper salts,

and other means must be devised. The usual methods adopted in the analyses described later are —

Reaction.	Indication of end.
1. Neutralization of acids and alkalis.	Using litmus, ¹ methyl orange, or phenolphthalein.
2. Ditto in presence of copper compounds.	Add alkali to solution. End of reaction marked by appearance of a faint turbidity, due to slight precipitation of copper compounds.
3. Estimation of KCN by standard AgNO_3 .	When all free KCN is absorbed, AgCN.KCN is decomposed with the formation of insoluble AgCN .
4. Estimation of copper by standard KCN.	When last trace of blue colour of ammonio compound just disappears.
5. Estimation of free KCN by standard ammonio copper solution.	By first appearance of permanent trace of blue colour.

Most of these changes are finally effected by the addition of even less than 0.05 c.c., and if the quantity of standard solution added amounts to about 25 c.c., the error occasioned by 0.05 c.c. is only one part in 500, and where several experiments are performed and the results averaged, this error may still further be diminished. Special attention will be directed to each indicator as its use is suggested.

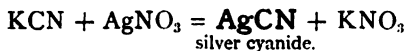
¹ Not if carbonic acid gas is present.

CHAPTER XXIII

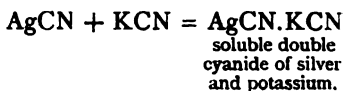
The Estimation of Cyanide

Necessity for the Test.—In almost all cyanide plating baths “free cyanide” is required to facilitate the solution of the anode. The correct amount to be used is a matter of opinion amongst different platers. There are limits within which the quantity should be kept, and which can be determined by a little experience. The allowable quantity may be expressed in terms of grams per litre, ounces per gallon, or even with respect to the metal content of the solution. Having a solution which by its working shows a suitable amount of free cyanide, some simple method is required by which the amount present may be estimated, so that as necessity arises, it may be brought up to its required value. Further, a few years ago cyanide itself was an uncertain substance. Many different grades were on the market at prices not so variant as quality. Now, merely looking at a sample of cyanide is a poor means of judging its value. Some simple test which can be applied in the workshop is necessary, and is also available.

The Reaction.—Take a small quantity of potassium cyanide solution in a test-tube, and add, drop by drop, with repeated shaking, a solution of silver nitrate (AgNO_3). Each drop of AgNO_3 produces a slight precipitate, which at first quickly redissolves in the cyanide. The following reaction is occurring :—



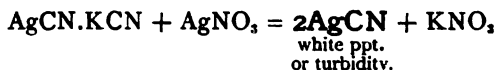
Then—



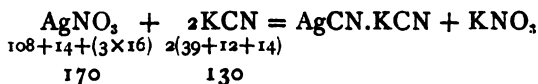
or, adding the two reactions, we have—



Continue this addition as long as the precipitate first formed redissolves. After a time this takes place only very slowly. At last a point is reached when the precipitate no longer redissolves, and, either as a slight precipitate or even as a turbidity, remains and is visible. This slight precipitate or turbidity marks the end of the reaction shown above, and the commencement of a new reaction as follows:—



This marks the important point at which there is no longer any free cyanide. Just at this point the silver nitrate added and the free cyanide in the solution have been in the proportion represented in the equation—



- Then for every 170 parts by weight of silver nitrate added there were 130 parts by weight of free potassium cyanide in the solution. Now, an easy way of determining the weight of AgNO_3 added would be to make a solution of definite strength, and observe the volume of the solution added, as indicated on p. 305.

Standard Silver Nitrate Solution.—Carefully weigh out 17 grams of silver nitrate. Dissolve in a little distilled water. Transfer to a litre measuring cylinder or flask, and by repeatedly washing the vessel in which the nitrate has been dissolved, and adding these washings to the solution, make

up the bulk of the solution to one litre. Use the best silver nitrate, and it will suffice for our purpose to regard this as pure. This is now a standard solution, that is, a solution of definite strength. Then—

1 litre of the solution contains 17 grams AgNO_3 ,
 \therefore 1 c.c. " " $\frac{17}{1000} = 0.017$ gram AgNO_3

But we have previously seen that when used as indicated above—

170 parts by wt. AgNO_3 — 130 parts by wt. of KCN

\therefore 1 part " " $\frac{130}{170}$ " "

and 0.017 gram AgNO_3 $\frac{130 \times 0.017}{170}$ gram KCN

Hence 1 c.c. of this AgNO_3 solution contains 0.017 gram AgNO_3 , and is capable of converting 0.013 gram KCN into the double cyanide of silver and potassium. Expressed briefly—

1 c.c. AgNO_3 soln. — 0.013 gram KCN

Transfer the standard AgNO_3 to a dry stoppered bottle, and label it—

Standard AgNO_3 ,
 1 c.c. — 0.013 gram KCN

Do not wash out the measuring flask or cylinder, and put the washings into the stoppered bottle, for this would at once alter the strength of the solution. The standard AgNO_3 solution should preferably be kept in an amber-coloured bottle, as silver salts are decomposed by light.

Estimation of Free Cyanide in a Silver-Plating Solution.—Rinse out a clean burette with distilled water, and then with a little of the standard AgNO_3 solution. Run

this solution out into the silver "residues." Fill up the burette with standard AgNO_3 , and, if necessary, run out again till the level stands at the zero mark.

By means of a pipette take several lots of 25 c.c. each of the silver-plating solution to be tested, into small round or conical flasks. Take one of them, and stand it on a dark surface under the burette. Very slowly add the AgNO_3 from the burette, and shake well after each addition. The test-tube experiment is now being repeated quantitatively. Usually a slight brown coloration is produced. Neglect this, and continue the addition of AgNO_3 , with shaking, until the permanent turbidity or faint insoluble precipitate is produced. Note the volume of AgNO_3 solution added, and record it. Refill the burette, and make the same test on two or three more samples of the plating solution. Any difficulty which may be experienced at first in judging the important end point of the reaction will disappear when several tests have been made. In all cases try to produce the same minimum precipitate or turbidity. Concordant results are necessary as a guarantee of accurate working. Typical results are shown as follows :—

C.c. plating solution.	C.c. standard AgNO_3 .	} Average = 17.5 c.c.
25	17.5	
25	17.6	
25	17.4	
25	17.5	

Hence it is found that 25 c.c. plating solution contain sufficient free cyanide to convert the AgNO_3 contained in 17.5 c.c. standard AgNO_3 into the double cyanide. Putting this another way we have—

$$\begin{aligned}
 &1 \text{ c.c. standard } \text{AgNO}_3 = 0.013 \text{ gram KCN} \\
 \therefore 17.5 \text{ c.c. } &,, \quad,, = 0.013 \times 17.5 \text{ gram KCN}
 \end{aligned}$$

Then as 25 c.c. plating solution require 17.5 c.c. of standard AgNO_3 to give the turbidity—

25 c.c. plating solution *contain* 0.013×17.5 gram KCN

1 c.c. " " contains $\frac{0.013 \times 17.5}{25}$ " "

1000 c.c. " " " $\frac{0.013 \times 17.5 \times 1000}{25}$ " "

(1 litre)

= 9.1 grams per litre

By this simple method, which with a little care can be performed by any workman, a fairly accurate estimate of the free cyanide in the silver plating solution can be made.

The silver nitrate solution may be kept for further tests, but it is better to make up a smaller quantity frequently, or as required, than attempt to keep a large quantity for months.

In each of these tests the flasks contain only double cyanide of silver and potassium. The liquid may at once be added to the silver bath, and no waste is incurred.

We imagine, however, that some would prefer to have the answer in terms of ozs. per gallon. This may be easily found, for there are 4.54 litres in a gallon, and 28.4 grams in an oz. (av). Hence—

$$\begin{aligned} & 9.1 \text{ grams in 1 litre} \\ & = 9.1 \times 4.54 \text{ grams in 1 gallon} \\ & = \frac{9.1 \times 4.54}{28.4} \text{ ozs. (av.) per gallon} \\ & = 1.45 \text{ ozs. per gallon} \end{aligned}$$

or more briefly still, grams per litre are converted to ozs. (av.) per gallon by dividing by 6.25. Thus, 9.1 grams per litre is equivalent to $\frac{9.1}{6.25} = 1.45$ ozs. (av.) per gallon.

A Less Refined Method.—The estimation of free cyanide in a plating bath need not be a matter of the *greatest* accuracy. It were better that it were done with cruder apparatus, than not done at all for the want of very accurate apparatus. The following method might therefore be carried out with dram, oz., and pint measures. Assuming that

gram weights are available with the balance, weigh out 9.66 grams of silver nitrate and dissolve in a little distilled water, and make up to one pint with distilled water. This solution is of approximately the same strength as the standard silver nitrate previously described.

1 fl. oz. AgNO_3 solution contains $\frac{9.66}{20} = 0.483$ gram AgNO_3 ,

which is equivalent to $\frac{130}{170} \times \frac{0.483}{1} = 0.37$ gram KCN

For the test on the plating solution take 2 fl. ozs. of the solution in a flask. Add the AgNO_3 solution from a fluid oz. measure on which the drams are marked. Shake after each addition, and continue addition and shaking until the permanent turbidity or slight precipitate is formed. Repeat several times, and note quantities used. Record as follows:—

Plating solution.		AgNO_3 solution.		
2 fl. ozs.	. . .	1 oz. 3	drams	} Average = 1 oz. 3 drams
2 "	. . .	1 "	2.5 "	
2 "	. . .	1 "	3.3 "	
2 "	. . .	1 "	3 "	

Then 1 fl. oz. $\text{AgNO}_3 \equiv 0.37$ gram KCN

\therefore 1 oz. 3 drams " $\equiv 0.37 \times 1\frac{3}{8} = 0.51$ gram

Hence—

2 fl. ozs. plating solution contain 0.51 gram
and 160 fl. ozs. (1 gallon) contain $0.51 \times 80 = 40.8$ grams
 $= \frac{40.8}{28.4} = 1.43$ ozs. (av.) KCN

NOTE.—The results here given were obtained in the manner shown, and it will at once be seen that for most ordinary purposes the cruder method will suffice.

Estimation of KCN in a Sample of Cyanide.—The foregoing method can now be applied to the determination of the value of any sample of cyanide, or, as it would be more

usually stated, to determine the percentage of KCN in the sample. When the sample is dissolved in water, it behaves in just the same way as free cyanide in a bath.

To be of any value this estimation should be done carefully.

Weigh out 5 grams of the sample to be tested. Transfer to a 250 c.c. flask. Dissolve in distilled water and make up the bulk to 250 c.c. Each 50 c.c. of this solution contains 1 gram of the sample. Assuming that the carefully prepared AgNO_3 solution (see p. 313) is still available, or that more has been made, fill up the burette with this solution and adjust the level to zero.

Take 25 c.c. of the solution of the sample in a flask, and, with all the usual precautions, run in AgNO_3 solution from the burette until the turbidity is obtained.

Repeat several times and record results as follows:—

Weight of sample taken, 5 grams. Dissolved and made up to 250 c.c.

C.c. KCN solution.	C.c. AgNO_3 solution.	
25	37.7	Average 37.6 c.c.
25	37.6	
25	37.6	
25	37.5	

Now 1 c.c. standard $\text{AgNO}_3 \equiv 0.013$ gram KCN

$\therefore 37.6$ " " " $\equiv 0.013 \times 37.6$ gram KCN
 $= 0.489$ gram KCN

$\therefore 25$ c.c. KCN solution contain 0.489 gram KCN

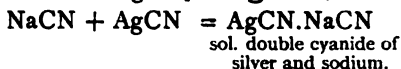
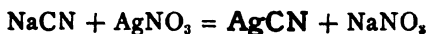
$\therefore 250$ " " " 4.89 " "

But 250 c.c. KCN solution contain 5 grams sample,

$\therefore 5$ grams sample contain 4.89 grams KCN

I	"	"	"	$\frac{4.89}{5}$	"	"
100	"	"	"	$\frac{4.89 \times 100}{5}$	grams KCN	
					$= 97.8$ per cent.	

Influence of Sodium Cyanide on the Results.—Now it sometimes happens that the final answer is more than 100 per cent. While this might seem impossible, still it can and does happen. In recent years commercial potassium cyanide has contained sodium cyanide. For all practical purposes the sodium cyanide is quite as effective as the potassium compound, and forms similar compounds, thus—



A comparison of the molecular weights of the two will show their quantitative difference—

$$\begin{array}{c} \text{KCN} \\ 39 + 12 + 14 \\ \hline 65 \end{array}$$

$$\begin{array}{c} \text{NaCN} \\ 23 + 12 + 14 \\ \hline 49 \end{array}$$

that is, for all purposes where cyanide is required, 49 parts by weight of sodium cyanide will do the same amount of chemical work as 65 parts by weight of the potassium compound.

Hence if sodium cyanide were tested with AgNO_3 under the supposition that it was potassium cyanide, then as—

$$\begin{aligned} 49 \text{ parts NaCN} &\equiv 65 \text{ parts KCN} \\ \therefore 100 \text{ ,, ,,} &\equiv \frac{65}{49} \times 100 \text{ parts KCN} \\ &= 132 \text{ KCN} \end{aligned}$$

and the sample would show 132 per cent. KCN. It will therefore be seen that if only a small percentage of the sodium compound occurs in the commercial cyanide, it may bring the percentage of KCN up to and exceeding 100, even when impurities are present. In fact, by the ordinary method of testing, a mixture of 75.5 per cent. NaCN, and 24.5 per cent. of impurities would, if reckoned as the potassium compound, show 100 per cent. strength.

Estimation of Free Cyanide in Copper Solutions.—This may be done by exactly the same method as that already described for silver-plating solution. The presence of copper (or zinc in a brassing solution) in no way interferes with the reaction. At the end of each test, however, the residue must not be added to the silver bath on account of the copper and other metals which may be present, but reserved as residues for the subsequent extraction of the silver.

Use of Blue Ammonio-Copper Solutions.—Reaction.—To a small quantity of copper sulphate solution add ammonia a little at a time. The green precipitate which first forms subsequently dissolves in more ammonia and gives the characteristic blue solution. If a cyanide solution is now added, it gradually removes the blue colour owing to the formation of colourless double cyanide of copper and potassium, and the end of the reaction, *i.e.* the disappearance of the last trace of colour, is very sharp. A method for estimating free cyanide can be based on this reaction. The blue ammonio-copper solution takes the place of the silver nitrate in the previous method. There is one important difference, however. There is not the definite relation between the copper in the blue solution and the free cyanide which decolorizes it, that exists between AgNO_3 and KCN . With AgNO_3 we can at once calculate the equivalent value of KCN for any given strength of nitrate solution. In the case of the blue copper solution, however, this must be experimentally determined, or, in other words, the blue copper solution must be "standardized," and this is done by means of a cyanide solution of known value.

Preparation of Blue Ammonio-Copper Solution.—Carefully weigh out 4 grams of electro-deposited copper (ordinary H.C. copper wire will do), dissolve in the minimum amount of nitric acid, and evaporate nearly to dryness to expel excess of acid. Dilute to 250 c.c. with water. Add ammonia till precipitate first formed is just redissolved.

Avoid excess of ammonia. Make up the bulk to 1000 c.c. A similar solution could be made by dissolving 15.75 grams of pure copper sulphate crystals, and subsequently treating with ammonia before making up to 1 litre.

Standardization of the Solution.—For this purpose a cyanide solution of known strength is required. Suppose we use the sample already determined on p. 317. It is not exactly pure—its purity being 97.8 per cent., that is, for every gram of sample there will only be 0.978 gram of the real KCN.

Weigh out 5 grams of the sample, dissolve in water, and make up to 250 c.c. in a measuring flask or cylinder. Shake in order that the solution shall be quite uniform in strength. Following the usual method, charge the burette with the blue copper solution. Take out several samples of 25 c.c. each of the cyanide solution, into round or conical flasks. Taking one sample, run in the blue copper solution a little at a time, shaking after each addition until a very faint violet colour just persists. After a few minutes this colour may disappear, but another drop of the blue solution should be added until the faint violet colour lasts for five minutes. Note the quantity of copper solution added. Repeat the experiment about three times, and aim at producing the same faint colour in each case. Record—

C.c. KCN solution.	C.c. Cu Solution.	
25	33.1	Average = 33.1 c.c.
25	33.0	
25	33.2	
25	33.1	

The strength of the copper solution in terms of KCN required to decolorize it will then be calculated as follows:—

Five grams sample KCN contain 4.89 grams of the real KCN (see p. 317).

\therefore 25 c.c. of the KCN solution contain 0.489 gram KCN

\therefore 33.1 c.c. Cu solution are decolorized by 0.489 gram KCN

\therefore 1 c.c. Cu solution is decolorized by and is $\equiv \frac{0.489}{33.1}$
 $= 0.0148$ gram KCN

Therefore, when using this blue copper solution, each c.c. used by the above method represents 0.0148 gram free KCN in the solution to which it is added.

The Estimation.—Take 25 c.c. of cyanide copper solution in a small flask. From the burette add the blue copper solution until a faint violet colour is produced and persists. Repeat three times and record as follows:—

C.c. Cu cyanide solution.	C.c. blue copper solution.	
25	45.5	Average = 45.6 c.c.
25	45.6	
25	45.7	
25	45.7	

Calculation—

Now, 1 c.c. blue copper solution \equiv 0.0148 gram KCN

45.6 c.c. " " " \equiv 0.0148 \times 45.6 gram KCN
 $= 0.675$ gram

\therefore 25 c.c. Cu cyanide bath contain 0.675 gram KCN

1 litre (1000 c.c.) contains $\frac{0.675}{25} \times 1000$ grams KCN
 $= 27$ grams

If this answer is required in terms of ozs. (av.) per gallon, divide by 6.25. Hence, one gallon of solution contains

$\frac{27}{6.25} = 4.3$ ozs. (av.) of free cyanide. The use of the ammonio-copper solution is not so accurate as silver nitrate, and with strong and impure solutions the end reaction is not so decided. The materials, however, are cheaper, and there is no mixing of silver and copper compounds, with the subsequent waste of the silver or the trouble of separation from the copper.

CHAPTER XXIV

Estimation of Constituents of Copper Solution

Introduction.—The metal content of a solution is an important item in the working of a bath. Many circumstances may cause its variation, the chief one being the efficiency or otherwise of the anode. Some anodes dissolve perfectly, such as copper, in the acid bath, and the metals in cyanide solutions, with a correct proportion of free cyanide. Moreover, it is important that the metal content should be kept at its highest value, especially where it is desirable to deposit the metal at a high rate, and to maintain at the same time a coherent deposit. Circumstances also arise in which it is desirable and necessary to know the actual amount of metal in a bath previous to setting it aside for the recovery of the metal. Methods of determining the metal content are capable of being carried out with fair accuracy with quite ordinary apparatus, though in some cases, where great accuracy is required, special apparatus is necessary, and must also be used with particular care.

The same or very similar methods apply also for the quantitative determination of the purity or otherwise of materials which are to be used in the workshop.

Specific Gravity Methods.—Where a solution contains only a single constituent, the amount of that substance can often be found by determining the specific gravity, and hence the proportion in which the constituent occurs by reference to an authoritative table. For example, the following are a few figures taken from a table which gives the relation of specific gravity and content of salt of a bluestone solution :—

TABLE XXXIII.

SPECIFIC GRAVITY OF COPPER SULPHATE SOLUTIONS.

Specific gravity.	Percentage of bluestone.	Specific gravity.	Percentage of bluestone.
1'0063	1	1'099	15
1'019	3	1'1354	20
1'032	5	1'174	25
1'045	7	1'215	30
1'065	10		

Hence, if a solution of bluestone has a specific gravity of 1'065, it contains 10 per cent. of its weight of bluestone.

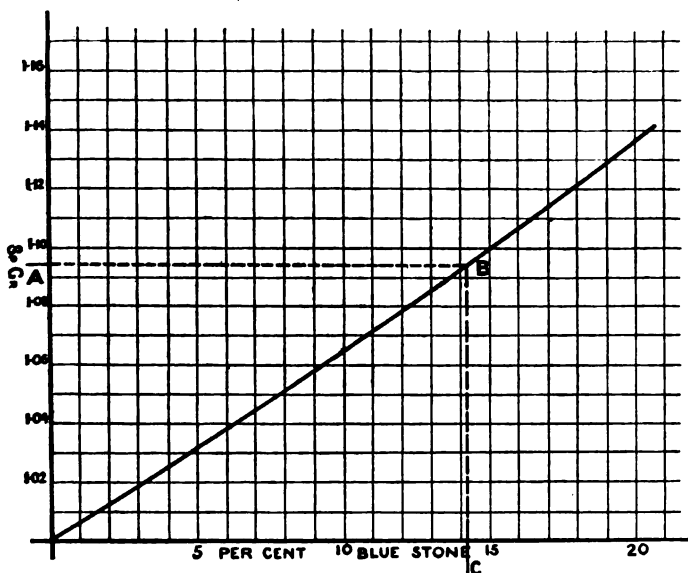


FIG. 116.—Specific gravity of copper sulphate solutions.

Hence, 10 grams of the salt are contained in 100'0 grams of solution, or 10 grams of bluestone with 90'0 grams of water,

or *about* 1 lb. per gallon. Again, if the specific gravity of another solution is 1.11, then the percentage of bluestone is more than 15, but less than 20. These intermediate values can only be obtained from a much more complete table, or by drawing a curve from the shorter table by the method described in Chapter XI. This curve is shown in Fig. 116, and the percentage of bluestone corresponding to a specific gravity of 1.095 is thus found to be 14.2.

For determining the specific gravity, the most accurate method would be that of the specific gravity bottle. Next to that would come the method of comparing the weights of equal volumes as measured by pipettes or burettes. Less accurate still are the methods using hydrometers, either direct reading or those which involve reference to a curve. This last method could only be used where an approximate result was required.

Solutions of more than One Substance.—The foregoing method applies only to solutions of a single substance. When two substances occur in the same solution, the method would be quite inapplicable. For example, in the acid copper bath the following mixtures all have practically the same specific gravity :—

Solution.	Sulphuric acid.	Bluestone.
	Grms. per litre.	Grms. per litre.
1	150	150
2	200	100
3	100	200
4	75	225

To use the specific gravity method would necessitate not merely one curve, such as is shown in Fig. 116, but quite a large number of these curves, showing the specific gravity of bluestone solutions when different quantities of acid are present. Then, after determining the amount of acid present by a chemical method, we might refer to the curve approximating most nearly to the amount, and so, roughly, compute the

percentage of bluestone present. Such a method is of no practical value, and nothing short of chemical analysis would serve the purpose.

Chemical Methods.—These, in many cases, are more simple than might be expected, but careful working is an essential to accurate results. They may be divided into two groups: (1) those in which the metal is actually extracted and weighed; and (2) those in which the metal is completely converted into some compound of definite composition, which is obtained in a pure form and weighed.

The latter method is more frequently used. For example, if to determine the amount of copper in a solution we can obtain the copper in the form of pure oxide (CuO) and weigh it, then we know that the oxide contains $\frac{63.6}{79.6} = 0.799$ of its weight of metal, and a simple calculation gives the result. Similarly, to determine the amount of H_2SO_4 in a solution containing no other sulphate, we might produce and obtain from it barium sulphate (BaSO_4). Then—

$$\begin{array}{rcc} \text{BaSO}_4 \text{ contains SO}_4 \text{ from H}_2\text{SO}_4 & & \\ 137+32+64 & 32+64 & 2+96 \\ 233 & 96 & 98 \end{array}$$

In other words, every 233 parts by weight of barium sulphate (pure) represent 98 parts by weight of H_2SO_4 in the solution.

The simple methods of quantitative analysis will now be explained in some detail for an acid copper solution, and subsequently the methods for other solutions can be described more concisely.

Estimation of Constituents of the Acid Copper Solution.—The two chief constituents are—

- (1) The copper, or the bluestone.
- (2) The *free* sulphuric acid.

It is not suggested that such estimations would have to be frequently made; but these methods are applicable to most

copper solutions which do not contain certain other metals, and any other free acid.

Estimation of Copper.

Outline of Methods.

(a) Those involving the precipitation of copper, and subsequently weighing the metal.

(1) By replacement with zinc.

(2) By electro-deposition, using a platinum anode.

(b) Those involving the conversion of the copper into compounds of definite composition.

(1) Conversion to oxide.

(2) Conversion to sulphide by precipitation with H_2S .

(3) Conversion to sulphide by precipitation with potassium sulphocyanide and sodium bisulphite.

(c) Volumetric methods, based on—

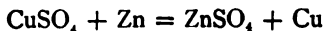
(1) The decoloration of blue ammonio solutions of copper with potassium cyanide.

(2) The liberation of iodine by the following reaction :—



and the subsequent estimation of the iodine by sodium thio-sulphate.

Precipitation by Zinc.—By means of a pipette take 25 c.c. of the acid copper bath. Transfer to an evaporating dish, and add *pure* granulated zinc or *pure* zinc foil. The following reaction at once occurs :—



and the copper may be completely precipitated by this method. If ordinary impure zinc is used, allowance should be made for the insoluble impurity which it contains. This usually amounts to 0.5–0.6 per cent. if not ignited, or 0.25 per cent. if it is heated to redness before weighing. The solution soon begins to lose its colour. Gently stir up the zinc with a

glass rod to separate off the precipitated copper. When the blue colour has entirely disappeared, add a little more acid (if necessary) to complete the solution of the zinc. When all effervescence has ceased, pour the clear liquid through a tared filter paper. Wash the precipitate in the dish several times with hot water, and decant the washings through the filter. Finally, wash the copper on to the filter, and continue washing until the washings give no turbidity with BaCl_2 solution. The copper has now to be dried and weighed. Carefully wash the copper and paper with the smallest amounts of alcohol (the industrial spirit will do for this purpose). Dry in a water or air oven, and weigh, placing the filter which does not contain the copper on the balance pan containing the weights. The weight of copper is thus directly obtained.

Example.—

Volume of solution used = 25 c.c.

Weight of copper obtained = 0.7123 gram

Hence if 25 c.c. contain 0.7123 gram Cu

1 c.c. contains $\frac{0.7123}{25}$ "

1000 c.c. contain $\frac{0.7123 \times 1000}{25}$ grams Cu

\therefore 1 litre of solution contains 28.49 grams copper

or 1 gallon contains $\frac{28.49}{6.25} = 4.55$ ozs. copper

These quantities multiplied by four give the corresponding amounts of bluestone.

Electrolytic Method.—This is a more refined method, demanding special apparatus. The apparatus is shown in Fig. 117. It consists of a platinum bowl about 8 cms. diameter and 4 cms. deep (Fig. 118). This is supported on a metal ring attached to the *glass* pillar of a suitable stand. It forms the cathode. After weighing the dish, 25 c.c. of the bath (which has first been diluted to one-quarter of its original strength)

are added, and diluted up to about 100 c.c. About 5 c.c. of strong nitric acid are added. The anode is formed (Fig. 119) by a spiral of platinum wire or a platinum bowl (Fig. 120). The anode is just lowered into the liquid, and the solution warmed to 50–60° C. The dish is covered with a watch-glass, through the centre of which a hole has been drilled; or, failing this, it will serve if the glass is fairly evenly broken into two parts. The connection is made to a 4 or 6-volt circuit, and a current of 0.5–0.8 ampere passed. Copper is at once

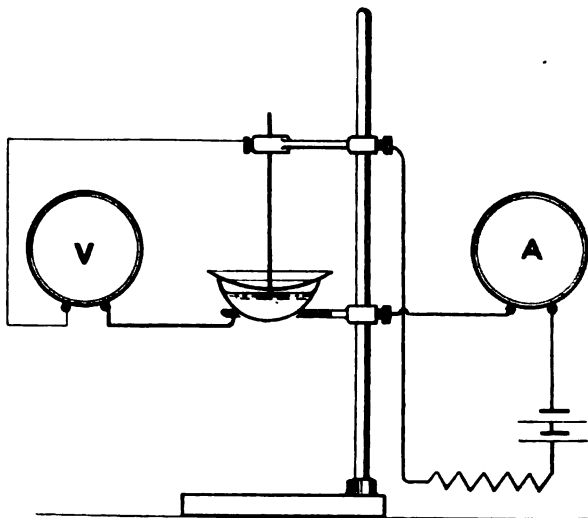


FIG. 117.—Apparatus for electrolytic analysis.

deposited on the platinum dish, and in a short time (depending upon the amount of copper present) the solution appears to be colourless and all the copper deposited. The last traces, however, are not easily deposited, and deposition must be allowed to go on for from three to five hours to completely deposit the copper. The test for complete deposition is made by taking out a few drops of the electrolyte, neutralizing with ammonia, and adding a few drops of H_2S solution. If a brown

coloration is produced, the whole of the copper is not yet deposited. The current may be increased to one ampere, and the experiment continued until, on testing, no brown coloration is produced. Switch off current; quickly pour away the electrolyte, and at once wash with a plentiful supply of hot distilled water. Finally, dry in a steam oven or over a small bunsen flame. The copper deposit should be untarnished, and this may be attained by rapid washing and quick drying. Weigh dish and deposit.



FIG. 118.—Platinum dish.

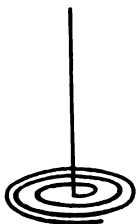


FIG. 119.—Spiral anode.

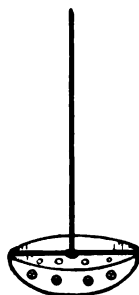


FIG. 120.—Bowl anode.

Example.—

Volume of diluted solution used = 25 c.c.

Weight of dish and copper = 25·8984 grams

Weight of dish alone = 25·7203 ,,

Weight of copper = 0·1781 gram

Hence weight of copper per litre of solution

$$= \frac{0\cdot1781}{25} \times 1000 \times 4 = 28\cdot5 \text{ grams}$$

or 4·55 ozs. per gallon.

Determination as Copper Oxide.—Take 25 c.c. of solution in a beaker (about 3 ins. diameter and 4 ins. deep); dilute with 100 c.c. water, and heat to boiling. Add a hot

clear solution of caustic soda or potash. A black precipitate is at once formed, and the alkali should be added until, after boiling and allowing to stand, the supernatant liquid is quite colourless. The whole of the copper is now precipitated as hydrated oxide. When the precipitate has settled, pour the clear liquid through a carefully folded filter paper in a funnel. Avoid getting the precipitate on the paper too soon. To the precipitate in the beaker add hot water; boil for a short time, and after settling pour the clear liquid through the paper. Repeat this operation two or three times and finally wash precipitate on to the paper, continuing washing until the washings show no turbidity with barium chloride solution. Dry. Transfer precipitate to a weighed porcelain crucible. Burn paper on to the inverted lid, and heat till all carbonaceous matter is burnt off. Cool. Moisten ash with a few drops of strong HNO_3 . Evaporate to dryness, and heat till residue is black. Place lid on crucible, and ignite for ten minutes. Cool and weigh.

Example.—

Volume of solution used = 25 c.c.

Weight of crucible, precipitate, and ash = 16.525 grams

Weight of crucible alone = 15.636 ,,

Weight of precipitate and ash = 0.889 gram

Weight of ash of paper = 0.001 ,,

Weight of CuO = 0.888 ,,

$$\text{Now, } \frac{\text{Cu}}{\text{CuO}} = \frac{63.6}{79.6}$$

$$\therefore \text{Cu in 0.888 gram CuO} = \frac{63.6}{79.6} \times 0.888 = 0.7095 \text{ gram}$$

\therefore 25 c.c. solution contain 0.7095 gram Cu

$$1 \text{ litre } ,, \text{ contains } \frac{0.7095 \times 1000}{25} = 28.38 \text{ grams Cu}$$

$$\text{And 1 gallon } ,, \text{ } ,, \frac{28.38}{6.25} = 4.53 \text{ ozs. Cu}$$

Estimation as Copper Sulphide.—The oxide method cannot be employed when the solution contains any other of the ordinary metals, such as zinc, iron, lead, mercury, nickel, etc. The method of precipitating the copper as sulphide makes it possible to estimate the copper even when the following ordinary metals are present: zinc, nickel, iron, aluminium, manganese, etc., and is therefore of much wider application.

For this estimation take 25 c.c. of the solution in a large beaker. Dilute to 150 c.c. with water. Warm to 50–60° C. Pass a stream of H_2S gas until the solution smells strongly of the gas. Warm again. Again pass the gas. Allow to settle, and filter rapidly. Wash by the usual method, using H_2S water instead of distilled water, and dry quickly. The precipitate should not be allowed to stand exposed to air for any length of time. Transfer precipitate to a weighed porcelain crucible; burn the paper to ash, and add the ash to the main precipitate. Add a little *pure* powdered sulphur, and place the lid on the crucible. Heat to redness in a flame which completely surrounds the crucible. Cool without removing the lid, and weigh. The residue is cuprous sulphide (Cu_2S) and ash.

Example.—

Volume of solution used = 25 c.c.

Weight of crucible, precipitate, and ash = 15.538 grams

Weight of crucible alone = 14.627 ,,

Weight of precipitate and ash = 0.911 gram

Weight of ash of paper = 0.001 ,,

Weight of Cu_2S = 0.910 ,,

$$\text{Then } \frac{Cu_2}{Cu_2S} = \frac{127.2}{159.2}$$

$$\therefore \text{Cu in precipitate} = \frac{127.2}{159.2} \times 0.910 = 0.726 \text{ gram}$$

Hence 25 c.c. solution contain 0.726 gram Cu

∴ 1 litre „ contains $\frac{0.726}{25} \times 1000 = 29.0$ grams Cu

And 1 gallon contains $\frac{29.0}{6.25} = 4.63$ ozs. Cu

Thiocyanate Method.—This method is of still wider application, and there are few metals which would ordinarily interfere with it.

Take 25 c.c. solution, and first neutralize the free acid by adding pure powdered sodium carbonate until a faint permanent precipitate is produced. This is then just redissolved by the addition of a few drops of dilute HCl. The solution now contains a minimum amount of free acid. It is heated to boiling, and a solution containing sodium bisulphite¹ (NaHSO₃) and potassium thiocyanate¹ (KCNS) is added until the liquid is colourless. The copper is precipitated as cuprous thiocyanate (CuCNS). It easily settles and filters, and is washed with facility. The washing must be done thoroughly. The subsequent treatment of the precipitate is the same as in the preceding case, the copper being finally weighed as Cu₂S. By heating—



Example.—

Volume solution used = 25 c.c.

Weight of crucible, precipitate, and ash = 12.9356 grams

Weight of crucible alone = 12.0493 „

Weight of precipitate and ash = 0.8863 gram

Weight of ash of paper = 0.0010 „

Weight of Cu₂S = 0.8853 „

¹ About 10 per cent. each reagent in the solution.

$$\therefore \text{weight of copper present} = \frac{127.2}{159.2} \times \frac{0.8853}{1} = 0.7084 \text{ gram}$$

$$\text{and 1 litre solution contains } 0.7084 \times \frac{1000}{25} = 28.34 \text{ grams}$$

$$\therefore 1 \text{ gallon contains } \frac{28.34}{6.25} = 4.52 \text{ ozs. Cu}$$

Volumetric Methods

I. Using Standard Potassium Cyanide.—A solution of potassium cyanide is prepared containing about 30 grams KCN per litre. It is to be used for decolorizing blue ammonio-copper solutions. It therefore needs to be standardized, that is, its power of decolorizing the blue copper compound must be accurately known. To determine this, weigh out accurately 1 gram of pure copper (good wire will serve), dissolve in a minimum amount of HNO_3 (1-1), and evaporate nearly to dryness to expel the acid. Redissolve in water, transfer solution to a 250 c.c. flask, and make up its volume to 250 c.c. *Shake well.* By means of a pipette take out three or four separate lots of 50 c.c. each into conical flasks. Using a moderately dilute ammonia, add sufficient to one of the flasks to just convert the copper salt into the clear blue solution; then add the same amount to each of the others.

Charge the burette with the KCN solution, and to one of the copper solutions run in the KCN solution until only a *faint* violet colour remains. This colour may be lost on standing. Note volume of cyanide used, and repeat with the other copper solutions. Record as follows:—

C.c. Cu solution.	C.c. KCN solution.	Average = 24.4 c.c.
50	24.5	
50	24.3	
50	24.4	
50	24.4	

Now, 50 c.c. Cu solution contain $\frac{50}{250} \times 1 = 0.2$ gram Cu

\therefore 24.4 c.c. KCN decolorize 0.2 gram Cu

\therefore 1 c.c. KCN decolorizes $\frac{0.2}{24.4} = 0.0082$ gram Cu

that is, when used in this manner, every c.c. of KCN solution will represent 0.0082 gram copper. It is essential that all these experiments should be conducted in as nearly the same manner as possible, and the solutions used in the subsequent estimation should contain approximately the same quantity of copper.

The Estimation.—Take 25 c.c. of the acid copper solution, and make up to 250 c.c. with water. It is thus reduced to $\frac{1}{10}$ of its strength. Of this dilute solution take four separate lots of 50 c.c. each. In each use the same minimum amount of ammonia to produce the clear blue solution. Using the standardized KCN from the burette, decolorize each solution, leaving as nearly as possible the same faint violet colour in each as was left in the standardization experiments. Record results as in the following example:—

C.c. diluted Cu solution.	C.c. standard KCN.	
50	18.0	} Average = 17.9 c.c.
50	17.9	
50	17.8	
50	17.9	

Now, 1 c.c. KCN solution $= 0.0082$ gram Cu

\therefore 17.9 c.c. „ „ $= 0.0082 \times 17.9$ gram Cu
 $= 0.1468$ gram

Hence 50 c.c. diluted Cu solution contain 0.1468 gram Cu

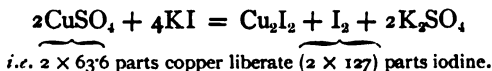
\therefore 250 c.c. „ „ „ 0.734 „

\therefore 25 c.c. ordinary „ „ 0.734 „

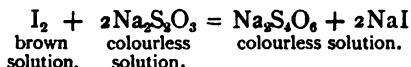
\therefore 1 litre „ „ contains 29.36 grams Cu

and 1 gallon contains $\frac{29.36}{6.25} = 4.7$ ozs.

II. Iodine Method.—This, as previously stated, is based on the following reaction :—



The iodine can readily be estimated by a standardized solution of sodium thiosulphate (hyposulphite), $\text{Na}_2\text{S}_2\text{O}_3$, thus—



Thiosulphate Solution.—Prepare a solution of sodium thiosulphate containing about 25 grams of the crystallized salt per litre. (This need not be accurately weighed, as the solution is subsequently standardized.) It is standardized with an iodine solution of accurately known strength. Prepare such a solution by dissolving 3.175 grams of iodine in water containing 10 grams of potassium iodide. (Iodine is more freely soluble in KI solution.) When dissolved, make up to 250 c.c.

Then 1 c.c. solution contains $\frac{3.175}{250} = 0.0127$ gram I

Take three or four separate lots of 25 c.c. each of the iodine solution in conical flasks. Fill up the burette in the usual manner with the “thio” solution, and add the thio drop by drop to one of the flasks containing the iodine solution. Shake after each addition. It will be observed that the iodine colour is rapidly lost. The solution becomes faintly yellow, and eventually one drop of thio will remove the last trace of colour. It must be done carefully. The end of this reaction may be made much sharper by the addition of a few drops of a solution of starch made by grinding 1 gram of starch with 100 c.c. water, and subsequently boiling. After allowing to settle, pour off the clear solution and use either in this or in a further diluted form. The addition of the starch

produces a very characteristic blue colour which is much more prominent than the light yellow colour of the iodine. Continue the addition of thio until this blue colour just disappears. Repeat with two or three other lots of iodine solution. Record as in the following example :—

C.c. iodine solution.	C.c. thio solution.	
25	24'0	} Average = 24'0 c.c.
25	24'1	
25	23'9	
25	24'0	

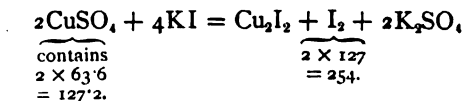
Then 250 c.c. iodine solution contain 3'175 gram I

∴ 25 c.c. „ „ „ 0'3175 „

∴ 24 c.c. thio are — 0'3175 gram I

and 1 c.c. thio — $\frac{0'3175}{24} = 0'01323$ gram I

As the thio solution is to be used on a copper solution it would be well to express its value in terms of copper. Thus from the equation—



Now, 254 grams I = 127'2 grams Cu

∴ 1 gram I = $\frac{127'2}{254}$ „

0'01323 gram I = $\frac{127'2}{254} \times 0'01323$ gram Cu

∴ 1 c.c. thio = 0'00662 gram copper

when used in the manner indicated above.

The Estimation.—For this purpose use the same diluted bath as before. Take four separate lots of 50 c.c. each, and add sodium carbonate powder until a faint permanent precipitate is formed. The purpose of this is to remove free mineral

acid, as this interferes with the reaction. Dissolve the faint precipitate in acetic acid, and add KI solution as long as a precipitate is formed. The precipitate is white cuprous iodide (Cu_2I_2), but coloured brown by the free iodine, and its presence does not interfere with the estimation of the iodine. Taking these tests separately, run in thio from the burette until the colour is nearly removed. Then add a few drops of the starch solution to obtain the blue colour, and continue the addition of thio until the colour disappears. Repeat with the other three samples, and tabulate results. The following are typical figures :—

C.c. diluted Cu solution.	C.c. thio solution.	
50	22'3	} Average = 22'27 c.c.
50	22'4	
50	22'2	
50	22'2	

Now, 1 c.c. thio = 0'00662 gram copper

∴ 22'27 c.c. thio = $22'27 \times 0'00662$ gram copper
= 0'147 gram

Hence 50 c.c. diluted copper solution contain 0'147 gram copper
and 1000 c.c. " " " 2'94 grams Cu

and 1 litre strong solution contains 29'4 grams Cu

that is, 1 gallon contains $\frac{29'4}{6'25} = 4'7$ ozs. (av.), and this is equivalent to about 1'15 lbs. bluestone.

Determination of Free Acid in Copper Bath.—

Free acid can readily be estimated volumetrically by neutralization with alkali. Sodium carbonate is suitable, but it must be pure, prepared by igniting pure sodium bicarbonate, when—

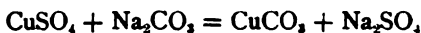


or it may be bought pure. With sulphuric acid it reacts thus—



The end of the reaction can usually be determined by means

of methyl orange, but such a change of colour would not easily be observed in the presence of coloured compounds. The end of the reaction can, however, be determined by the formation of a light green turbidity, indicating the complete neutralization of the acid and the beginning of the precipitation of copper as carbonate—



To apply this principle, prepare a **standard sodium carbonate** solution by dissolving 2.65 grams of pure Na_2CO_3 in distilled water, and making up to 250 c.c.

Then 1 c.c. Na_2CO_3 solution contains 0.0106 gram Na_2CO_3 ,

$$\begin{array}{rcl} \text{But} & \text{Na}_2\text{CO}_3 & \equiv \text{H}_2\text{SO}_4 \\ & (2 \times 23) + 12 + 48 & 2 + 32 + 64 \\ & 106 & \equiv 98 \end{array}$$

Now, 106 grams $\text{Na}_2\text{CO}_3 \equiv 98$ grams H_2SO_4

$$1 \text{ gram} \quad \quad \quad \equiv \frac{98}{106} \text{ gram}$$

$$0.0106 \text{ gram} \quad \quad \equiv \frac{98}{106} \times 0.0106 \text{ gram } \text{H}_2\text{SO}_4$$

\therefore 1 c.c. Na_2CO_3 solution \equiv 0.0098 gram H_2SO_4

The Estimation.—Take three or four lots of 25 c.c. each of the diluted copper bath in conical flasks. Charge the burette with the standard sodium carbonate solution. Add the Na_2CO_3 solution slowly to the copper solution, shaking after each addition. A slight precipitate may soon form, but will redissolve. The experiment must be finished at the first sign of a *permanent* turbidity. Do the same with the other three samples, and record:—

C.c. diluted Cu solution.	C.c. Na_2CO_3 solution.	Average = 13.54 c.c.
25	13.55	
25	13.5	
25	13.6	
25	13.5	

Now, 1 c.c. standard $\text{Na}_2\text{CO}_3 \equiv 0.0098$ gram H_2SO_4

$\therefore 13.54$ c.c. „ „ $\equiv 0.0098 \times 13.54$ gram H_2SO_4
 $= 0.1327$ gram

$\therefore 25$ c.c. diluted bath contain 0.1327 gram H_2SO_4

$\therefore 1000$ c.c. „ „ „ 5.308 „ „

and —

1 litre strong solution contains $5.308 \times 10 = 53.1$ gram H_2SO_4

From this it will be seen that 1 gallon of the solution contains $\frac{53}{6.25}$ ozs. $\text{H}_2\text{SO}_4 = 0.53$ lb. per gallon. Such a result is based on the assumption that the whole of the acid is H_2SO_4 , which would usually be the case.

Methods of quantitative analysis have thus been shown in their application to the acid copper bath. The methods are simple, but a little experience is required in order to acquire confidence and accuracy, and the results then become far more accurate and reliable than the specific gravity methods and crude hydrometer tests. Other metals will be dealt with in a succeeding chapter.

CHAPTER XXV

Further Examples of Quantitative Estimations

Estimation of Silver.—Where silver is being used in any quantity, it becomes a matter of importance to avoid waste. The silver contents of the plating solution, the composition of silver alloys, the contents of silver in shop-dirt—these are matters on which a “quantitative eye” should be kept. In most cases the method is simple, and it is only necessary to exercise moderate care to obtain a good idea of the amount of metal present.

Simple Method.—In solutions which do not contain cyanide, silver is precipitated with dilute hydrochloric acid as silver chloride (AgCl). The only metals which interfere are lead and mercury as mercurous salts. These, as a rule, are not present, except perhaps in negligible quantities, and even if present in small quantities the lead can be eliminated by taking advantage of the solubility of its chloride in hot water.

To take a simple case. Suppose it is required to determine the strength of a given solution of nitrate of silver. Transfer 25 or 50 c.c., according to its probable strength, to a beaker. Warm and add a slight excess of dilute HCl , that is, till no further precipitate is produced. The precipitate is heavy, and gentle stirring and warming causes the precipitate to clot together, and this facilitates filtration. A folded filter paper is now carefully fitted into a funnel, and while still warm the clear liquid is poured through by means of a glass rod. When practically the whole of the clear liquid has thus been filtered,

the precipitate remaining in the beaker is washed with hot water. The washings are similarly poured through the filter and the washing repeated several times. Finally the precipitate is washed on to the paper, care being taken that no fine particles remain in the beaker. A wash-bottle is useful for the purpose of detaching such particles from the side and bottom of the beaker and of washing them on to the filter paper. The precipitate is now dried by placing the funnel containing the precipitate either in an air oven at about 105°C. , or even over a small bunsen flame, so that in drying, the paper may not be scorched. The precipitate is next transferred as *completely as possible* into a clean and carefully weighed porcelain crucible. The paper is then folded and supported by means of a platinum wire, as shown in Fig. 111, and burned, and the ash allowed to fall on the inverted lid of the crucible. When cool it is moistened with nitric acid (1-1), and a few drops of dilute hydrochloric acid added and slowly evaporated to dryness, carefully avoiding spitting. When dry the lid is replaced on the crucible and gently heated until the chloride shows first signs of fusion. It is then entirely free from moisture, and is cooled and weighed.

Example.—

Volume of solution used = 25 c.c.

Weight of crucible and precipitate = 14.284 grams

Weight of crucible alone = 14.107 „

Weight of silver chloride = 0.177 gram

Now, silver chloride = AgCl.
 $108 + 35.5 = 143.5$

143.5 parts silver chloride contain 108 parts of Ag

\therefore 1 part „ „ contains $\frac{108}{143.5}$ „

\therefore 0.177 gram AgCl contains $\frac{108}{143.5} \times \frac{0.177}{1}$

= 0.133 gram of silver

Hence, 25 c.c. solution contain 0.133 gram Ag

$$\therefore 1000 \text{ ,, ,, ,, } \frac{0.133}{25} \times 1000 \\ = 5.32 \text{ grams silver}$$

Estimation of Silver in a Plating Solution.—The above method requires but little modification when dealing with a plating solution. In this case a rather larger volume of strong hydrochloric acid is necessary to effect precipitation, because (1) the free cyanide present must be first decomposed, (2) silver cyanide is next precipitated, and this needs converting to the chloride, and (3) other metals present, for example, copper, would be precipitated as single cyanides with the silver, but would be converted to soluble chlorides with the stronger acid when warmed, thus leaving the silver chloride pure, and making the estimation more accurate. The process is then continued as in the case of a simple nitrate solution.

Example.—

Volume of plating soln. used = 25 c.c.
 Weight of crucible and precipitate = 13.961 grams
 Weight of crucible alone = 13.594 ,,
 Weight of silver chloride = 0.367 gram

$$\begin{aligned} \text{Weight of Ag} &= \frac{108}{143.5} \times \frac{\text{weight of chloride}}{1} \\ &= \frac{108}{143.5} \times \frac{0.367}{1} = 0.276 \text{ gram} \end{aligned}$$

Hence, 1 litre solution contains $0.276 \times 40 = 11.04$ grams metal

and 1 gallon contains $\frac{0.276 \times 4540}{25} = 50$ grams

$$= \frac{50}{30.5} = 1.64 \text{ ozs. (troy)}$$

Further Methods.—(1) Another method available is that of evaporating 25 or 50 c.c. to dryness in a large porcelain

crucible or small porcelain evaporating dish. When dry, a mixture of sodium carbonate and nitre is added and the whole well fused. The silver compounds are reduced to metal, which collects in the form of one or more small beads. By cooling, and boiling with water these can be obtained, dried, and weighed. The nitre serves to oxidize other metals present and thus to eliminate them.

(2) The following method is due to Mr. A. H. Allen, of Sheffield. A measured quantity of the solution is diluted and dilute acid (HNO_3 , HCl , or H_2SO_4) added until a permanent precipitate just begins to form. The solution is now boiled and saturated with H_2S . The silver is precipitated as Ag_2S (also copper if present). It is filtered and washed, again transferred to a beaker, and warmed with bromine water, bromine being added if necessary. Copper thus goes back into solution while the sulphide of silver is converted to bromide (AgBr), which is obtained in a similar manner to the chloride. Then—

$$\frac{\text{Ag}}{\text{AgBr}} = \frac{108}{108 + 80} = \frac{108}{188} = 0.574$$

(3) In another method, suggested by Mr. T. J. Baker, of Birmingham, combining accuracy and simplicity with rapidity, 20–50 c.c. of the solution are treated with dilute nitric acid. This throws down the silver as cyanide and also the copper, and the precipitate is filtered, washed, and dried as usual. The precipitate is then transferred on to some thin sheet assay lead.¹ The paper is burned and the ash added to the precipitate. As an alternative, the paper and precipitate may be wrapped up in the lead at once. The lead is now rolled up and compressed to a small compass, and cupelled.

[Note on Cupellation.—Bone ash, which consists chiefly of calcium phosphate, when heated, readily absorbs oxide of lead. Thus, if a little lead is heated on a small vessel called a cupel (Fig. 121), made of bone ash, the metal melts and oxidizes, and

¹ Lead free from silver.

the oxide is absorbed by the bone ash, and nothing remains but a yellow or orange stain. None of the other ordinary metals does this, but when mixed with comparatively large amounts



FIG. 121.—
Cupel.

of lead and heated on a cupel, the metallic oxides are dissolved by the fused litharge and are carried by it into the cupel. As silver and gold do not oxidize by simply heating in air, they cannot be cupelled, that is, they are not absorbed by the cupel, however much lead may be used. Again, if silver or gold contain impurities, they may be entirely freed from them by cupelling with sufficient lead to take off these impurities. Thus a little ordinary sterling silver, containing copper, when cupelled with lead, loses the copper, and silver remains behind in a pure form, and this principle is used considerably in both the estimation of silver and gold in their alloys, and also in the extraction of these precious metals from their ores.]

The reaction depends upon the easy decomposition of silver cyanide when heated, the silver being absorbed by the molten lead and finally remaining as a single bead on the cupel, when the lead has been absorbed. On cooling, the bead of silver is freed from any particles of bone ash, and weighed. It will be observed that copper is eliminated by being carried into the cupel by the lead.

Estimation of Gold in Gilding Solutions.—In determining the amount of gold present in a gilding solution or other liquid, it is the invariable practice to obtain the metal, and this usually by a very direct process. The following process was described by Mr. A. H. Allen, many years ago.

A quantity of the gilding solution is carefully evaporated in a porcelain crucible or dish to a syrupy liquid. It is then mixed with litharge (lead oxide, PbO), and the evaporation continued to dryness. The mixture contains chiefly gold cyanide, potassium cyanide, and litharge. The temperature is then raised, when the gold cyanide is readily decomposed, and the potassium cyanide reduces the lead oxide to metal, which at

once absorbs the gold. The temperature is maintained for some time and the button of lead obtained after cooling. From this the gold may be obtained either by treating the lead with nitric acid, in which it is dissolved, leaving the gold, or by the process of cupellation.

Silver solutions could be similarly treated, but the final separation of lead and silver could not be easily effected by nitric acid without further precipitating the chlorides. Cupellation is much more direct.

Ferrous Sulphate Method.—A quantity of the gilding solution, 25–50 c.c., is first freed from cyanides by boiling with strong HCl, which converts the metals into chlorides. The gold is now precipitated free from the other metals by the addition of a *clear* solution of ferrous sulphate (FeSO_4).



The reaction is slow, and the mixture is allowed to stand in a warm place for about twenty-four hours, after which it is filtered, washed, and dried. If the paper and precipitate is now burned to ash in a clean weighed porcelain crucible, the gain in weight at once shows the amount of gold present. As only a very small amount of gold is obtained, care would have to be taken to make due allowance for the weight of the filter paper ash, which, while negligible in larger precipitates, would become important in this case.

Estimation of Copper in Cyanide Solutions.—Methods for the estimation of copper in acid solutions have been somewhat fully described in the previous chapter, and it only remains to point out here that cyanide solutions need first to be boiled with excess of hydrochloric or sulphuric acid to get rid of cyanides, after which the general methods may be followed.

Estimation of Zinc.—From solutions of the sulphate and similar salts the following method serves to determine the metal content. Solutions of cyanides should first be boiled with acid, as in the case of copper. The zinc is then usually

precipitated as carbonate. This is done by means of sodium carbonate, which, as the solutions to which it is to be added are usually acid, may be added little by little in the form of powder. This avoids a large increase in the bulk of the solution which would be caused by adding a dilute solution. In either case no permanent precipitation occurs until the whole of the acid is neutralized, after which zinc carbonate of uncertain composition is precipitated. Boiling facilitates settling. Filtering is a slower process than in the case of silver or many of the copper compounds, and washing must be done most thoroughly on account of the large quantity of sodium chloride or sulphate formed in neutralizing the excess of acid with sodium carbonate. When the washings give no further test for chloride or sulphate, as the case may be, the precipitate is dried. Further precautions are required when burning the paper. After transferring the precipitate to a weighed porcelain crucible, the filter paper is moistened with a strong solution of ammonium nitrate, and again dried. It is then burned and the ash added to the precipitate. In the process of burning the filter paper, the zinc carbonate (say, ZnCO_3) becomes converted to oxide (ZnO), which may be reduced by the carbon and gases from the paper to zinc, and this being volatile, may escape, involving loss. Ammonium nitrate, on heating, readily gives up nitrous oxide (N_2O), which is strongly oxidizing. It therefore promotes the rapid burning of the paper, and prevents the reduction of the zinc oxide. The crucible now contains a carbonate of indefinite composition, but by strongly heating for five or ten minutes, it is converted into the oxide (ZnO) of definite composition. From the weight of oxide the weight of zinc can be readily calculated for—

$$\frac{\text{Zn}}{\text{ZnO}} = \frac{65}{65 + 16} = \frac{65}{81} = 0.802$$

Analysis of a Brassing Solution.

(A) **Free Cyanide** may be determined by either of the methods described in Chapter XXIII.

(B) **The Metals.**—Several methods are suitable, according to whether one or both metals are required. In any case, the solution used is boiled with HCl or H_2SO_4 to convert the cyanides into chlorides or sulphates, and to get rid of free KCN .

(1) **ELECTROLYTIC METHOD.**—While decomposing cyanides the liquid is evaporated down to a small bulk, until it becomes syrupy. It is then diluted with water to about 50 c.c., and washed into a weighed platinum dish (see p. 328). The solution is then diluted further, if necessary, and 5 c.c. of strong nitric acid added. From the warm solution the copper is deposited out with a low E.M.F. When the solution is quite colourless, tests are made on the *smallest* drops of the liquid, to ascertain if the deposition is complete. The zinc present does not interfere with the end test. When finished, the liquid is transferred quickly but carefully to a beaker, and the dish rinsed out with distilled water, adding the rinsings to the solution. The dish is quickly dried and weighed. The weight of the copper is thus obtained. From the solution the zinc can be determined by precipitating with sodium carbonate, as on p. 346, or by converting to the double oxalate with ammonium oxalate and electrolyzing it to obtain the zinc.

(2) A method wholly chemical consists of precipitating the copper from the acid solution with sulphuretted hydrogen, as described on p. 331. The zinc remains in solution, and after the filtrate and washings have been boiled to get rid of excess H_2S , the zinc can be precipitated as carbonate and weighed as oxide.

Analysis of Brass Deposits or Anodes.—If the behaviour of a brassing solution is being carefully investigated, information regarding the composition of both anode and deposit must be obtained. Such information is not difficult to obtain. The analytical methods can now be applied on both anode and deposit. In each case, if we make the assumption that only two metals are present—copper and zinc—the analysis is reduced to a determination of only *one* of the two constituents,

the one which is most easily and accurately made. The copper is usually determined. Moreover, methods must be selected which will not be interfered with by the presence of zinc. For this purpose the following methods are available:—Electrolytic, sulphide with H_2S in acid solution, thiocyanate and iodine methods.

In the case of an anode, about 0.5 gram is dissolved in the smallest amount of nitric acid in a covered beaker or dish, and the solution evaporated to a syrup. It is then diluted and submitted to one of the methods above mentioned.

In the case of a deposit it is essential that this should be made on a metal like platinum, which will withstand the action of nitric acid. After the weight of the deposit has been determined, it can be removed by covering with warm acid in a shallow dish. Its removal is quickly effected, after which the platinum cathode must be well washed with distilled water, the washings falling into the nitric acid solution. After drying, the weight of the cathode can be again taken in order to ascertain for certain that the whole of the deposit has been removed. The solution is then evaporated nearly to dryness, diluted, and the copper determined. Then—

$$\frac{\text{wt. of copper}}{\text{wt. of alloy}} \times 100 = \text{percentage of copper}$$

$$100 - \text{percentage of copper} = \text{percentage of zinc}$$

Estimation of Iron.—The following is a simple method and one which is capable of application in many cases, for example, in the steel-facing solution, in the acid copper or nickel baths, or in bluestone or nickel salts. An essential condition is that the iron shall first be obtained in the ferric form, and this is usually done by boiling the solution with a little strong nitric acid (see p. 277). In carrying out the method, to 25 or 50 c.c. of the solution, dilute sulphuric acid is added with a few drops of strong nitric acid, and the solution boiled for a short time. The ferrous salts are converted to ferric compounds, which are subsequently more

easily precipitated and washed. After cooling, an excess of ammonium chloride and ammonia solution are added, the mixture is boiled for a short time, allowed to settle, filtered, washed, dried, and ignited in a crucible. The residue is Fe_2O_3 . This method would not be well applied in estimating iron in the presence of a preponderance of copper. It would be much preferable to eliminate the copper first, by precipitating with H_2S , and, after filtering and boiling off excess of H_2S , to oxidize with nitric acid, and proceed with the estimation as before.

Estimation of Nickel.—The nickel content of a bath may be arrived at by several methods.

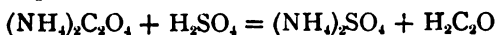
(1) **Specific Gravity Method.**—If the solution is one containing one substance only, either the single sulphate or double sulphate, then an approximate idea of its composition and content of nickel can be gained from the specific gravity as determined by the use of the specific gravity bottle. The method would not be applicable for mixtures of the double and single salts. Under all ordinary circumstances chemical methods would be required.

(2) **Estimation of Nickel in Pure Solutions.**—With no other metal present, nickel can readily be determined by—

(a) The caustic soda method, already detailed for copper (see p. 330). The nickel precipitate is first green, but after ignition is changed to black oxide (NiO), from the weight of which the amount of nickel present is easily calculated, thus—

$$\frac{\text{Ni}}{\text{NiO}} = \frac{58.6}{74.6} = 0.785$$

(b) The electrolytic method is also available on the condition that the solution does not become acid. The decomposition of nickel sulphate from either single or double salts would induce acidity, but this can be obviated by the presence of a salt like ammonium oxalate, from which the sulphuric acid liberates oxalic acid, which does not interfere with the deposition, thus—



From such a solution the nickel can be completely deposited and weighed.

(3) **Nickel Solutions containing other Metals.**—Should iron be present in the nickel solution, it would be precipitated and deposited in the foregoing methods with the nickel, and, in the case of the caustic soda method, the weight of the ignited precipitate would be due to $\text{NiO} + \text{Fe}_2\text{O}_3$. Without attempting to determine both metals from the same portion of solution, the iron, which is possibly present only in small quantity, may be determined as follows:—

To the measured volume of solution (25–50 c.c.) add an excess of ammonium chloride solution, followed by ammonia till the liquid smells strongly of ammonia. Boil for a short time. Of the two metals only iron is precipitated, and it can at once be filtered, washed, dried, ignited, and weighed as Fe_2O_3 . It is safer, however, when separating a small constituent from a larger one, to redissolve the precipitate $[\text{Fe}_2(\text{OH})_6]$ from the paper, and reprecipitate the iron, a more complete separation being thus effected. Then—

$$\text{Wt. of NiO} = (\text{wt. of NiO} + \text{Fe}_2\text{O}_3) - (\text{wt. of Fe}_2\text{O}_3)$$

from which the metal contents are calculated.

(4) **Copper in Nickel Solution.**—A very small proportion of copper in a nickel bath exerts a very detrimental effect on the character of the deposit, and in indicating the manner in which it can be determined we are at the same time dealing with other cases of the separation of copper and nickel. The nickel solution containing copper (or solution of a nickel copper alloy, for example, German silver, which also contains zinc) is first acidified, and, after warming, saturated with H_2S . The copper is precipitated, filtered, washed, dried, and weighed as Cu_2S , as described on p. 331.

Estimation of Tin.—This may sometimes be required in tracing the change of strength of a tinning or bronze solution, or the proportion of tin in a deposited alloy, such as bronze. Almost invariably the estimation involves the conversion of

the metal or compound into the oxide SnO_2 , which can readily be obtained in a pure form convenient for weighing. Moderately strong nitric acid directly converts the metal into a white insoluble powder, which, although its composition may be open to doubt, is converted to the definite oxide SnO_2 by heat. The same reaction occurs when any alloy containing tin is treated with the acid, and this renders the estimation of tin in its alloys a matter which does not present great difficulty.

Estimation of Tin in Bronze.—Bronze is an alloy of copper and tin, the tin usually not exceeding 20 per cent. 0.5–1.0 gram is weighed, and introduced into an evaporating dish, and covered with water. Strong nitric acid is added a little at a time, and heat applied until the action is complete. Copper passes into solution, and tin remains as an insoluble and almost white powder. The liquid is boiled for a short time, allowed to settle, filtered, and the precipitate washed thoroughly with hot water. While the precipitate is on the paper it is moistened with warm dilute nitric acid, to ensure the complete removal of copper. After washing again with water, the precipitate is dried and transferred to a weighed crucible, and the paper burned to ash on the inverted lid. When cool, it is moistened with strong nitric acid, and slowly evaporated to dryness. The lid is placed on a crucible and heated strongly for five to ten minutes. After cooling, it is weighed, the residue being SnO_2 .

$$\text{Then } \frac{\text{Sn}}{\text{SnO}_2} = \frac{118}{118 + 32} = \frac{118}{150} = 0.787$$

By such a method tin can be estimated in bronze anodes or deposits, while the filtrate containing copper and other metals may be examined further if required.

Estimation of Tin in Solutions.—Tinning solutions, as will be learned from Chapter XV., usually contain either alkaline or ammonium compounds, the tin compound used being either the protochloride (stannous chloride, SnCl_2), or the dioxide (SnO_2). When such solutions are acidified

and saturated with H_2S , the tin is precipitated either as stannous sulphide (SnS), which is of a dark brown colour, or stannic sulphide (SnS_2), as a yellow precipitate. The precipitation is effected in a warm solution, and after filtering, the precipitate is washed with a solution of H_2S . The precipitate is then dried, transferred to a weighed crucible, the ash of the paper being added. Care should be taken to fold the paper so that the precipitate remaining on it will be well inside, as, if tin comes into contact with platinum, it alloys with it.

The precipitate should now be gently heated in the open crucible. The sulphides burn, and, losing sulphur, are converted to oxide. To ensure complete conversion the precipitate is moistened with strong HNO_3 , and carefully evaporated to dryness, and ignited. After cooling, it is weighed as SnO_2 .

CHAPTER XXVI

Recovery of Metals

Introduction.—As a number of the materials which are in common use in electroplating are of considerable value, and as in course of time contamination with impurities renders them unfit for use, the necessity arises for recovering the valuable constituents in a form which admits of their being worked up again. Thus a silver-plating or gilding solution may become unfit for use after a time, and the gold and silver are too costly to waste. Again, stripping solutions for these metals soon contain sufficient valuable metal to justify its recovery. In fact, the very dirt in a polishing shop where gold and silver goods are treated may often contain sufficient metal to pay for extraction.

General Principles.—It will be obvious that such methods of extraction will depend largely upon the materials to be treated, and even then the methods suggested below may require modification for special circumstances. In any case, the recovery may be carried out with one of the two following objects :—

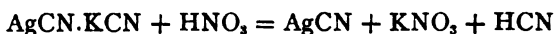
- (1) The extraction of the metal in a pure form, or
- (2) The formation of a pure compound of the metal which can subsequently be worked up again into a solution.

Thus, following method 1, gold and silver are readily obtained from their compounds, while, as examples of method 2, silver chloride might be made from waste silver materials and at once worked up by cyanide into a plating solution. Similarly for

a disused nickel solution, while no attempt is ever made at actually recovering the nickel as metal, it is well within the bounds of practicability to obtain from it a fair proportion of its double salt. Further, it will be noticed that the methods suggested for recovery are on somewhat similar lines to those already described for the estimation of the materials, and, indeed, in many cases are but the application of these methods to larger masses of materials. It is, however, highly desirable that the metal or compound obtained should be as pure as possible, and attention to some details at certain steps in the process serve to ensure this.

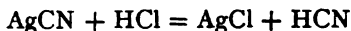
Recovery of Silver.—A number of important principles are applied in the extraction of this metal, and may first be described.

(1) From all cyanide solutions of silver the cyanide is precipitated by dilute acid, thus—

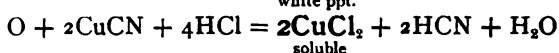
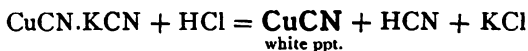


This occurs on account of the decomposition of the KCN which holds the AgCN in solution. Such an operation should, therefore, be conducted in a fume cupboard or in a well-ventilated place, in order that the very poisonous fumes of hydrocyanic acid may readily escape.

(2) If strong hydrochloric acid is used and the mixture heated, the single cyanide of silver is converted to chloride.



(3) If copper is present in the silver solution it behaves similarly to silver in the first stage and different from it in the second.



Boiling the solution with strong acid, therefore, effects the separation of silver and copper.

(4) The silver chloride can easily be washed and dried or

dissolved again to produce a new plating solution, though some **may** not be in favour of this method, objecting to the use of **the chloride**. No hesitation, however, should be shown in **thus** utilizing this substance.

(5) Silver chloride can be readily reduced to the metallic **state** if a sufficiently high temperature is forthcoming. When **heated** with sodium carbonate the metal is obtained thus—



Application of these Principles.

(A) **Recovery of Silver from an old Solution.**--

(1) Such a solution would be too bulky to treat directly with **acid**. Evaporation to a small bulk in as simple and convenient a manner as possible is desirable. This may be done by a coil of lead-pipe through which waste steam passes. Once **started**, the evaporation needs no further attention. The **small** bulk of solution is now transferred to a stone-ware tank surrounded by hot water for precipitation with acid. The utmost care should be taken to avoid inhaling the fumes **evolved**. An enamelled iron kettle is useful for the precipitation, but may not always be available. Common hydrochloric acid only need be used, and of this a Winchester quart ($= \frac{1}{2}$ gallon) should cost only about sixpence. It is added till no further precipitation occurs. The silver is then in the solid precipitate, and to this more acid is added, and the mixture warmed and stirred. The silver chloride is heavy and soon sinks, leaving a clear liquid above. Warming and stirring facilitates the separation of the silver chloride. After allowing to settle, practically the whole of the liquid can be poured away without appreciably disturbing the precipitate. The precipitate is, however, contaminated with the impurities of the residual liquid, but these being soluble may be washed away. The precipitate is now washed with water—tap water will serve—stirred, allowed to settle, and the water again poured off as completely as possible. The operation is

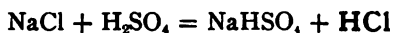
repeated and the silver chloride obtained sufficiently pure for most purposes. It may now be dried and preserved, or worked up to a new solution if thought desirable, or reduced to the metal by the following method. A clay crucible of convenient size is heated in a coke or good gas furnace, and a quantity of borax added. The borax first swells up, effervesces, and finally runs down as a clear colourless liquid. The crucible should now be turned about until the melted borax has run over the whole of the inside, any excess being poured off. On cooling, the crucible will be found to be glazed inside, this being done to prevent particles of silver from sticking to it. The dried silver chloride is now mixed with about six times its weight of sodium carbonate, and a small quantity of nitre added. The mixed materials are charged into the hot crucible, which is then put back into the furnace. When a good red heat has been obtained, a brisk effervescence is seen to be taking place. When this ceases, and the fused mass is quiet, the whole is poured out into a previously warmed iron mould. A good red heat should be maintained during the heating, as the melting point of silver is nearly 1000°C . The addition of nitre serves to ensure the final oxidation of other metals which may have persisted in the silver chloride. The silver obtained can then be remelted and poured into cold water to granulate it and render it more suitable for dissolving in acid. It should be clean and white.

(2) Another method which may be followed involves evaporating the solution completely to dryness and fusing the residue with sodium carbonate in a glazed crucible. The method is open to the objection that the whole of the impurities in the solution are introduced into the last stage of the process, and are therefore more difficult to eliminate.

(B) **Recovery from Residues.**—Wherever silver compounds are being used, it is necessary to save the materials and recover the silver. There should thus be kept a jar or bottle labelled "Silver Residues," into which they can be

thrown. Common hydrochloric acid is added at intervals to precipitate the silver as chloride or cyanide, after which the clear liquid can be thrown away, and thus the silver from a large amount of compounds is collected in a small compass. The extraction of the silver is then carried out as described above by treating these solid residues with more strong acid to ensure that the cyanides of other metals which may occur are decomposed, the metals passing into solution.

(C) **From Acid Stripping Liquids** the silver may be recovered by diluting, adding hydrochloric acid to precipitate the chloride, and continuing the method as before. In this case the addition of common salt would effect the precipitation, as by contact with sulphuric acid it at once liberates hydrochloric acid, thus—



(D) **From Shop Dirt.**—The method of extraction of silver from shop dirt is substantially that used also for gold, and is described under that heading.

Recovery of Gold.—Owing to its high cost this metal must be extracted from liquids and residues in which it occurs in only very small quantity. In order not to treat solutions of large bulk, ordinary methods of concentration should be adopted, it being remembered that a given amount of gold will be more completely and easily recovered from a small bulk of strong solution than a larger bulk of proportionately weaker solution.

(A) **Recovery of Gold from Solutions.**—Very many methods are available, among them being the following:—

(1) The gold cyanide is first precipitated with dilute hydrochloric acid, due care being exercised with regard to the fumes. The acid should be added carefully in order to avoid excess. The precipitate is allowed to settle, subsequently pouring off the clear liquid and washing the precipitate. The dried precipitate is then treated by one of the following methods:—

(a) By mixing with sodium carbonate and a little nitre, and fusing in a glazed clay crucible, the gold compounds are readily decomposed even at a low temperature, but on account of the high melting point of gold, viz. 1065°C. , a good red heat must be maintained to completely fuse the metal and render its collection as a single bead or ingot more easy.

(b) The gold compound, after drying, is wrapped in thin sheet lead, and the whole cupelled. If sufficient lead is used, then pure gold remains on the cupel, though if silver is originally present it still occurs in the gold, but is separated from it when the gold is subsequently dissolved in *aqua regia*.

(2) From most dilute solutions of gold the metal may be effectively thrown down by ferrous sulphate or green vitriol (FeSO_4). The precipitation takes some considerable time, but is usually very complete. Acid solutions are preferable, as cyanide solutions are not acted upon by this salt, and the method is therefore applicable to diluted stripping solutions. Then—



the gold being precipitated as a fine powder. It is subsequently washed and obtained by fusion with sodium carbonate and nitre, or by cupellation with lead.

(3) Similar reduction of gold compounds to the metallic state occurs by the addition of zinc, either in the form of filings or other finely divided condition. The precipitated gold is thus mixed with zinc, from which mixture the zinc may be dissolved with acid and thus separated from the insoluble gold.

(4) A simple method of obtaining gold from cyanide solutions is that of deposition. Using a carbon or platinum anode and a thin gold or platinum cathode, a large proportion of the gold may be obtained by deposition in the form of an adherent deposit. From the platinum cathode it could not be dissolved by *aqua regia*, as platinum is also dissolved by this mixture of acids, but it can be worked again into a gilding solution by using it as the anode until the

gold has entirely disappeared. The method is open to the error that towards the end of the deposition other metals which may be present as impurities are simultaneously deposited, but a considerable proportion of the gold is obtained by this simple deposition method, and the residual solution used for the electrolytic stripping of gold from old deposits.

Recovery of Gold from Sweep.—This method may be used for silver in a similar manner, and also where the two metals occur together. The sweep contains a large amount of organic matter, and also a large proportion of oxide of iron, alumina, and silica, from the polishing materials. The organic matter is first burnt off in a furnace, and the bulk of the sweep is reduced considerably during this operation. In the next stage the residue is mixed with a flux containing a large proportion of carbonate of potash with common salt and red lead, and fused in a clay pot. The carbonate of potash being very fusible forms fusible compounds with the impurities and produces a slag by combining with the impurities. Residual organic matter is oxidized by the oxygen from the red lead, and the lead resulting from this reaction absorbs the gold and silver, forming a very fusible alloy. After pouring into a mould, the slag and alloy are easily separated, and the gold and silver obtained by scorification, cupellation, and (if necessary) parting.

Separation of Silver and Gold—"Parting."—By several of the foregoing methods, silver and gold may be obtained together, and must be separated. The separation is based on the fact that silver is dissolved by nitric acid, while gold is not. If an alloy of the metals containing a distinctly larger proportion of silver than gold is treated with nitric acid, the silver dissolves and the gold remains, usually as a dark powder. Several important points have to be observed. If a small amount of silver is contained in a large amount of gold, it is manifestly impossible for the acid to enter into the mass of the metal to dissolve out the silver. If the proportions are reversed, then as the larger quantity of silver is dissolved

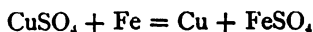
away, the mere skeleton of gold which remains readily falls to a powder, and thus the action occurs throughout the mass of the metal. If the proportion of silver to gold is less than $2\frac{1}{2} : 1$, this separation or "parting" is not easily effected, and in order to bring about the separation it is necessary to melt the alloy with sufficient silver to give this proportion of $2\frac{1}{2} \text{ Ag} : 1 \text{ Au}$. In order to attack the alloy more readily, it should be rolled and then wound into a convenient spiral form. The acid used contains strong pure acid (HNO_3) and distilled water in equal volumes. When the action has ceased, the silver nitrate can be obtained from the liquid by evaporation and crystallization, and used for the preparation of a plating solution, while the gold which is in the form of a dark powder is washed, dried, and gently heated. It then assumes its usual yellow colour, and is in a convenient form for preparing a new solution.

Recovery of Copper.—Seldom is it necessary to extract metals from other plating solutions. With the acid copper bath, for example, practically no change of composition should occur over extended periods of working. Further, as has already been shown, the presence of impurities in moderate quantity in this solution has very little effect on the deposit. Seldom, if ever, does it become necessary to recover the metal or salts. In special circumstances, however, the following methods might prove of some use :—

(1) Evaporation by waste steam or other means to recover a large proportion of the sulphate as crystals.

(2) Deposition of most of the copper on thin sheets of copper, using carbon or lead anodes. Slow deposition would produce a coherent deposit which could be afterwards used as an anode in a new solution.

(3) The copper might also be obtained by means of scrap iron by simple replacement—



but while the method has some considerable application in other directions it could hardly be of use to the plater.

The Recovery of Nickel presents a more reasonable demand owing to the difference between its price and that of its compounds and those of copper. Further, where a small amount of nickel in an acid copper bath would be quite harmless, the same amount of copper in a nickel bath would play havoc with the deposit. The problem of the recovery of nickel salts cheaply is therefore one of practical importance. The presence of copper, moreover, may accidentally happen, perhaps unsuspectingly by leakage through imperfect woodwork between the two adjacent vats, or by careless or accidental addition of copper sulphate to the nickel solution. These are things which may happen. A 200-gallon tank of nickel solution containing $\frac{3}{4}$ lb. of double salts per gallon contains 150 lbs. of the double salts, which at 4d. per lb. represents about 50s. This sum need not be thrown away too readily by scrapping the solution. Slow evaporation by waste steam would effect some precipitation. This may easily be increased by the addition of a moderate quantity of ammonium sulphate costing, say, 15s. per cwt., and thus a considerable amount of the double salts could be obtained, leaving a small proportion behind in the solution with the impurities. Other considerations, such as the time involved, labour, and convenience, would perhaps weigh heavily against the above, but the method becomes more practicable with richer solutions containing single salts.

It will be remembered that copper may be separated from nickel for analytical purposes by acidifying and passing H_2S , or by electro-deposition, but these methods could not be easily applied commercially.

APPENDIX

General Information

- 1 inch = 2·54 centimetres.
- 1 foot = 0·3048 metre.
- 1 yard = 0·9144 „
- 1 metre = 39·37 inches.
- 1 sq. inch = 6·45 sq. cms.
- 1 sq. foot = 9·28 sq. dm.
- ∴ C.D. per sq. foot = C.D. per sq. dm. \times 9·28.
- 1 gramme = 15·43 grains.
- 1 pound (av.) = 7000 grains.
- 1 „ = 453·6 grammes.
- 1 ounce (av.) = 28·4 „
- 1 „ (troy) = 31·1 „
- 1 pennyweight (dwt.) = 1·555 grammes.
- 1 kilogramme = 2·205 lbs. (av.).
- 1 gallon = 160 fl. ozs.
- 1 pint = 20 fl. ozs.
- 1 litre = 35·2 „
- 1 gallon = 4·536 litres.
- 1 „ = 4536 c.c.
- 1 pint = 567 c.c.
- 1 fl. oz. = 28·4 „
- 1 litre = 1·76 pints.
- 1 cu. ft. water weighs 62·5 lbs.
- 1 gallon „ „ 10 lbs.
- ∴ 1 cu. ft. water = 6·25 gallons.
- 1 „ „ = 28·4 litres.
- 1 coulomb = 1 ampere-second.
- 1 ampere-hour = 3600 coulombs.
- 1 gramme equivalent is deposited by 96,540 coulombs.
- 1 „ „ „ 26·8 ampere-hours.

1 pound (av.) equivalent is deposited by 12,150 ampere-hours.

1 watt = 1 volt ampere.

1 horse-power = 746 watts.

1 horse-power hour deposits $\frac{746}{26.8 \times V}$ gramme equivalents,

where V = voltage used.

1 Board of Trade Unit (B.T.U.) = 1000 watt-hours
= about $1\frac{1}{3}$ horse-power hours.

1 litre hydrogen at N.T.P. weighs approx. 0.09 gramme.

1 gramme hydrogen at N.T.P. = 11.11 litres.

1 gramme molecular weight of any gas at N.T.P. occupies
22.22 litres.

TABLE XXXIV.
THE CHIEF ELEMENTS.

Element.	Symbol.	Metal (M) or Non-metal (N).	Atomic weight.	Valency.
Aluminium	Al	M	27	3
Antimony	Sb	M	120	3 & 5
Argon	A	—	39·9	—
Arsenic	As	—	75	3 & 5
Barium	Ba	M	137	2
Bismuth	Bi	M	208	3
Boron	B	N	11	3
Bromine	Br	N	80	1
Cadmium	Cd	M	112·4	2
Calcium	Ca	M	40	2
Carbon	C	N	12	4
Chlorine	Cl	N	35·5	1
Chromium	Cr	M	52	3
Cobalt	Co	M	59	2
Copper	Cu	M	63·6	1 & 2
Fluorine	F	N	19	1
Gold	Au	M	197	1 & 3
Hydrogen	H	—	1·008	1
Iodine	I	N	127	1
Iron	Fe	M	56	2 & 3
Lead	Pb	M	207	2 & 4
Lithium	Li	M	7	1
Magnesium	Mg	M	24	2
Manganese	Mn	M	55	2
Mercury	Hg	M	200	1 & 2
Nickel	Ni	M	58·7	2
Nitrogen	N	N	14	3 & 5
Oxygen	O	N	16	2
Phosphorus	P	N	31	3 & 5
Platinum	Pt	M	195	4
Potassium	K	M	39	1
Silicon	Si	N	28	4
Silver	Ag	M	108	1
Sodium	Na	M	23	1
Strontium	Sr	M	87·6	2
Sulphur	S	N	32	2, 4 & 6
Tin	Sn	M	118	2 & 4
Zinc	Zn	M	65	2

TABLE XXXV.

COMMON AND CHEMICAL NAMES AND FORMULÆ OF SUBSTANCES.

Common names.	Chemical names.	Formula.
Oil of vitriol . . .	Sulphuric acid . . .	H_2SO_4
Aqua fortis . . .	Nitric acid . . .	HNO_3
Spirits of salt } Muriatic acid }	Hydrochloric acid . .	HCl
Blue-stone or } Blue vitriol }	{ Crystallized copper sulphate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
White vitriol . . .	Crystallized zinc sulphate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Green vitriol . . .	Crystallized ferrous sulphate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Caustic potash . . .	Potassium hydrate . .	KOH
„ soda . . .	Sodium hydrate . . .	NaOH
Soda ash . . .	Sodium carbonate . . .	Na_2CO_3
Washing soda . . .	„ „ crystals	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
Bicarbonate of soda .	„ hydrogen carbonate	NaHCO_3
Common salt . . .	„ chloride . . .	NaCl
Glauber salt . . .	„ sulphate . . .	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
Epsom salt . . .	Magnesium sulphate . .	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Single Nickel salt . .	Nickel sulphate . . .	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
Double Nickel salt . .	Nickel ammonium sulphate	$\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
Lunar caustic . . .	Silver nitrate . . .	AgNO_3
Sal-ammoniac . . .	Ammonium chloride . .	NH_4Cl
Nitre or } Saltpetre }	Potassium nitrate . . .	KNO_3
Chili saltpetre . . .	Sodium nitrate . . .	NaNO_3
Quicklime . . .	Calcium oxide . . .	CaO
Chalk . . .	„ carbonate . . .	CaCO_3
Slaked lime . . .	„ hydrate . . .	$\text{Ca}(\text{OH})_2$
Spirits of hartshorn .	Ammonium hydrate . . .	NH_4HO
Vinegar . . .	Acetic acid . . .	$\text{HC}_2\text{H}_3\text{O}_2$
Spirits of wine . . .	Ethyl alcohol . . .	$\text{C}_2\text{H}_5\text{O}$
Ether . . .	Diethyl ether . . .	$\text{C}_2\text{H}_5\text{O}$
Borax . . .	Sodium baborate . . .	$\text{Na}_2\text{B}_4\text{O}_7$
Argol } Cream of tartar }	{ Potassium hydrogen tartrate	$\text{KHC}_4\text{H}_4\text{O}_6$
White arsenic . . .	Arsenious oxide . . .	As_2O_3

TABLE XXXVI.

SPECIFIC GRAVITY OF SULPHURIC ACID SOLUTIONS AT 15° C.

Specific gravity.	Percentage of H_2SO_4 .	Specific gravity.	Percentage of H_2SO_4 .
1'0064	1	1'306	40
1'013	2	1'351	45
1'019	3	1'398	50
1'0256	4	1'448	55
1'032	5	1'501	60
1'039	6	1'557	65
1'0536	8	1'615	70
1'068	10	1'675	75
1'083	12	1'734	80
1'114	16	1'786	85
1'144	20	1'822	90
1'182	25	1'8376	95
1'223	30	1'8426	100
1'264	35		

TABLE XXXVII.

SPECIFIC GRAVITY OF HYDROCHLORIC ACID SOLUTIONS.

Specific gravity.	Percentage of HCl.	Specific gravity.	Percentage of HCl.
1'200	40'8	1'098	20
1'197	40	1'074	15
1'174	35	1'064	13
1'164	33	1'054	11
1'154	31	1'0437	9
1'141	28'5	1'0318	6'5
1'131	26'5	1'026	5'3
1'118	24'0	1'020	4
1'108	22	1'012	2'5

TABLE XXXVIII.

SPECIFIC GRAVITY OF NITRIC ACID SOLUTIONS AT 15° C.

Specific gravity.	Percentage of HNO ₃ .	Specific gravity.	Percentage of HNO ₃ .
1'530	100	1'304	48
1'516	96	1'284	45
1'509	94	1'264	42
1'495	90	1'251	40
1'478	85	1'225	36
1'470	83	1'198	32
1'460	80	1'185	30
1'442	75	1'172	28
1'423	70	1'138	23
1'405	66	1'120	20
1'395	64	1'089	15
1'386	62	1'077	13
1'374	60	1'067	11'4
1'346	55	1'045	7'2
1'335	53	1'022	4
1'317	50	1'010	2

TABLE XXXIX.

SPECIFIC GRAVITY OF COPPER SULPHATE SOLUTIONS.

Specific gravity.	Percentage of Bluestone.	Specific gravity.	Percentage of Bluestone.
1'0126	2	1'1208	18
1'0254	4	1'1354	20
1'0384	6	1'1501	22
1'0516	8	1'1659	24
1'0649	10	1'1817	26
1'0785	12	1'1980	28
1'0923	14	1'2146	30
1'1063	16		

TABLE XL.
SPECIFIC GRAVITY OF ZINC SULPHATE SOLUTIONS.

Specific gravity.	Percentage of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.	Specific gravity.	Percentage of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.
1'0115	2	1'156	25
1'023	4	1'1914	30
1'035	6	1'2285	35
1'0467	8	1'267	40
1'059	10	1'308	45
1'090	15	1'351	50
1'122	20	1'396	55

TABLE XLI.
SPECIFIC GRAVITY OF POTASSIUM CYANIDE SOLUTIONS.

Specific gravity.	Percentage of KCN.	Specific gravity.	Percentage of KCN.
1'013	2	1'089	15
1'025	4	1'1195	20
1'036	6	1'149	25
1'048	8	1'181	30
1'061	10	1'213	35

TABLE XLII.
SPECIFIC GRAVITY OF AMMONIA SOLUTIONS AT 14° C.

Specific gravity.	Percentage of NH_3	Specific gravity.	Percentage of NH_3
0'996	1	0'9414	15
0'987	3	0'925	20
0'979	5	0'911	25
0'971	7	0'898	30
0'959	10	0'886	35
0'952	12		

TABLE XLIII.
COMPARISON OF HYDROMETER SCALES.

Specific gravity.	Beaumé.	Twaddell.	Specific gravity.	Beaumé.	Twaddell.
1'000	0	0	1'195	24	39
1'007	1	1'4	1'215	26	43
1'014	2	2'8	1'235	28	47
1'020	3	4	1'278	32	55'6
1'028	4	5'6	1'324	36	64'8
1'034	5	6'8	1'375	40	75
1'041	6	8'2	1'428	44	85'6
1'057	8	11'4	1'485	48	97
1'072	10	14'4	1'546	52	109
1'088	12	17'6	1'615	56	123
1'104	14	20'8	1'690	60	138
1'121	16	24'2	1'771	64	
1'138	18	27'6	1'864	68	
1'157	20	31'4	1'960	72	
1'176	22	35'2			

TABLE XLIV.
COMPARISON OF THERMOMETRIC SCALES.

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
- 10	14	75	167
- 5	23	80	176
0	32	85	185
5	41	90	194
10	50	95	203
15	59	100	212
20	68	150	302
25	77	200	392
30	86	300	572
35	95	400	752
40	104	500	932
45	113	600	1112
50	122	700	1292
55	131	800	1472
60	140	900	1652
65	149	1000	1832
70	158	1200	2192

TABLE XLV.

PERCENTAGES OF METALS IN COMPOUNDS.

Compound.	Formula.	Constituent.	Percentage.
Cupric oxide	CuO	Cu	79.90
Cuprous sulphide	Cu ₂ S	Cu	79.90
Silver chloride	AgCl	Ag	75.26
" "	AgCl	Cl	24.74
Zinc oxide	ZnO	Zn	80.25
Nickel oxide	NiO	Ni	78.58
Ferric oxide	Fe ₂ O ₃	Fe	70.0
Aluminium oxide	Al ₂ O ₃	Al	52.94
Barium sulphate	BaSO ₄	SO ₄	41.20
" "	BaSO ₄	S	13.73
Lead sulphate	PbSO ₄	Pb	68.32
" oxide	PbO	Pb	92.82
Stannic oxide	SnO ₂	Sn	78.66

TABLE XLVI.

SPECIFIC GRAVITY AND WEIGHT OF METALS.

Metal.	Specific gravity or weight of 1 c.c. (gms.).	Weight of 1 cu. inch (ozs. av.).
Aluminium	2·6	1·5
Antimony	6·7	3·9
Copper	8·9	5·15
Gold	19·3	11·1
Iron	7·8	4·5
Lead	11·4	6·6
Magnesium	1·6	0·925
Mercury	13·6	7·9
Nickel	8·3	4·8
Platinum	21·5	12·4
Silver	10·5	6·05
Tin	7·4	4·26
Zinc	6·9	3·98

TABLE XLVII.

MELTING-POINTS OF METALS AND COMMON SUBSTANCES.

Metals and Substances.	Melting-point ° C.	Metals and Substances.	Melting-point ° C.
Sodium	95	Magnesium	633
Sulphur	115	Aluminium	657
Lithium	180	Potassium chloride	740
Silver nitrate	218	Sodium chloride	770
Tin	232	Sodium carbonate	818
Bismuth	266	Silver	961
Cadmium	322	Gold	1065
Lead	327	Copper	1084
Zinc	420	Manganese	1245
Silver chloride	451	Nickel	1450
Borax	561	Iron	1500
Antimony	630	Platinum	1770

TABLE XLVIII.

THICKNESS OF WIRES.

Standard wire-gauge (S.W.G.).	Diameter.	
	Inch.	Centimetre.
0	0'340	0'855
1	0'300	0'762
3	0'259	0'658
5	0'220	0'560
7	0'180	0'457
10	0'134	0'341
12	0'109	0'277
14	0'083	0'210
16	0'064	0'162
18	0'048	0'122
20	0'036	0'0915
22	0'028	0'071
24	0'022	0'056
26	0'018	0'046
28	0'0148	0'038
30	0'0124	0'032

TABLE XLIX.
RESISTANCE OF METALS AND ALLOYS.

Substance.	Relative conductance.	Specific resistance (microhms).
Silver	100	1'6
Copper	100	1'6
Gold	78	2'06
Aluminium	55	2'9
Magnesium	36	4'4
Zinc	28	5'75
Platinum	19	8'2
Iron	16'7	9'6
Nickel	13	12'3
Lead	7'5	20'0
Antimony	4'3	35'0
Mercury	1'6	100
Bismuth	1'2	130
Manganin	3'0	53'3
Platinoid	3'75	42'5
German silver	5'0	32

TABLE I.
RESISTANCE OF ELECTROLYTES.

Substance.	Specific resistance. ¹	Temperature ° C.
Copper sulphate (sat.)	29'3	10
Zinc " "	33'7	10
" " "	21'5	14
Potassium sulphate "	16'6	10
Sodium chloride "	4'7	18
Potassium bichromate "	29'6	10
Sulphuric acid (1'2)	8'0	12
Nitric acid (1'36)	1'4	—

¹ Specific resistance—ohms per cm².

TABLE LI.
RESISTANCE OF WIRES.

Metal.	S.W.G.	Ohms per foot.	Feet per ohm.
Copper	12	0'000944	1060
	14	0'001595	628
	16	0'00249	402
	18	0'00443	226
	20	0'00787	127
	22	0'013	77
	24	0'021	47'5
Iron	12	0'00566	177
	14	0'00957	105
	16	0'01496	67
	18	0'0266	37
	20	0'0472	21
German silver	12	0'0189	53
	14	0'0319	31
	16	0'0498	20
	18	0'0886	11'3
	20	0'1574	6'3
Platinoid	20	0'21	475
Manganin	20	0'262	3'8

TABLE LII.
ELECTRO-CHEMICAL EQUIVALENTS, ETC.

Element.	Chemical equivalent.	Electro-chemical equivalent (milligrams).	Grammes deposited per ampere-hour.	Ozs. (av.) per 746 ampere-hours.
Aluminium	9	0'0931	0'334	8'8
Antimony	40	0'414	1'49	39'4
Copper(ic)	31'8	0'329	1'182	31'2
„ (ous)	63'6	0'658	2'364	62'5
Gold(ic)	65'7	0'68	2'44	—
„ (ous)	197	2'04	7'35	—
Hydrogen	1	0'01035	0'0373	0'985
Iron	28	0'29	1'04	27'4
Lead	103'5	1'07	3'85	101'0
Magnesium	12	0'124	0'447	11'8
Mercury(ic)	100	1'035	3'72	98
„ (ous)	200	2'07	7'45	196
Nickel	29'35	0'302	1'085	28'6
Silver	108	1'118	4'025	—
Tin(ous)	59	0'61	2'19	57'8
„ (ic)	29'5	0'305	1'095	28'9
Zinc	32'5	0'336	1'21	32

TABLE LIH.

WEIGHTS OF SUBSTANCES DECOMPOSED PER AMPERE-HOUR.

Substance.	Formula.	Molecular weight.	Equivalent weight.	Grammes decomposed per ampere-hour.
Acetic acid . . .	$\text{HC}_2\text{H}_3\text{O}_2$	60	60	2.24
Hydrochloric acid . .	HCl	36.5	36.5	1.36
Nitric acid . . .	HNO_3	63	63	2.35
Sulphuric acid . . .	H_2SO_4	98	49	1.83
Zinc sulphate . . .	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	287	143.5	5.35
Ferrous sulphate . .	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	139	5.18
Nickel sulphate . . .	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	281	140.5	5.24
Copper sulphate . . .	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	249.6	124.8	4.65
„ cyanide . . .	CuCN	89.6	89.6	3.33
Silver cyanide . . .	AgCN	134	134	5.00
„ nitrate . . .	AgNO_3	170	170	6.33
Gold chloride . . .	AuCl_3	303.5	101.7	3.78
„ cyanide . . .	AuCN	223	223	8.31
Double cyanide of Ag and K . . .	AgCN.KCN	199	199	7.42
Double cyanide of Au and K . . .	AuCN.KCN	288	288	10.72
Double cyanide of Cu and K . . .	CuCN.KCN	154.6	154.6	5.75
Stannous chloride . .	SnCl_2	189	94.5	3.52

TABLE LIV.

WEIGHT AND THICKNESS OF METALS DEPOSITED OR DISSOLVED BY 10 AMPERES PER SQUARE FOOT.

Metal.	Grammes per 10 ampere-hours.	Inch thickness per hour with 10 amp./sq. foot.
Copper (sulphate) . . .	11.82	$0.000561 = \frac{1}{1780}$ approx.
„ (cyanide) . . .	23.64	$0.001122 = \frac{1}{890}$ „
Zinc . . .	12.1	$0.00074 = \frac{1}{1350}$ „
Gold (chloride) . . .	24.5	$0.000535 = \frac{1}{1870}$ „
„ (cyanide) . . .	73.5	$0.001605 = \frac{1}{623}$ „
Silver . . .	40.25	$0.001610 = \frac{1}{621}$ „
Iron . . .	10.4	$0.000564 = \frac{1}{1770}$ „
Tin (stannous) . . .	21.9	$0.001250 = \frac{1}{800}$ „
„ (stannic) . . .	10.95	$0.000625 = \frac{1}{1600}$ „
Nickel . . .	10.85	$0.000552 = \frac{1}{1813}$ „
Lead . . .	38.5	$0.001430 = \frac{1}{700}$ „

¹ The denominator of the fraction shows the number of hours required to obtain a thickness of one inch.

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